Journal
of
The Franklin Institute
Devoted to Science and the Mechanic Arts

Vol. 208 SEPTEMBER, 1929 No. 3

ACOUSTICAL CONTROL OF THEATRE DESIGN.

BY

HEREWARD LESTER COOKE,

Professor of Physics, Princeton University.

THIS paper contains an account of the fundamental principles which must be conformed to in the design of an auditorium or theatre in order to bring about a prearranged distribution of sound intensity throughout the audience. The method to be described differs from those employed at present in that the desired distribution of sound is first decided on and the form of the hall then worked out, step by step, so as to effect the prearranged acoustical result, instead of first choosing the form of hall as determined by architectural and practical considerations, and then testing the design to ascertain what acoustical results are to be anticipated. Acoustically, the present method represents the logical line of attack on the problem. In practice it is found to lead to a form of hall well in agreement with the trend of modern theater and auditorium design. There appears to be no conflict whatever between the best acoustical design and architectural considerations.

The nature of the proposed solution of the problem may be understood by considering the matter in a general way. Suppose that the plan of the hall and stage has been decided on from practical considerations, and the form and position of the audience surfaces fixed. Imagine now that the hall has been built with the walls in position, the building being

left open to the sky. Sound originating from the stage will then proceed to the audience area by direct line transmission and by reflection from the wall and floor surfaces. Knowing the form and acoustical properties of these surfaces a reasonably accurate calculation can be made of relative intensity of the sound received at all parts of the audience areas. This intensity will be found to differ widely in different regions. Since no ceiling is in position a large part of the sound energy originating at the stage will radiate into the open and be lost. The proportion of the total energy escaping in this manner can be estimated with considerable accuracy. Suppose now that this lost energy could be controlled by reflection at a ceiling and redirected to the audience areas in any manner desired. It is obvious that it would then be possible to distribute this sound energy over the audience so that at no point would the total intensity of sound received fall below some calculated minimum.

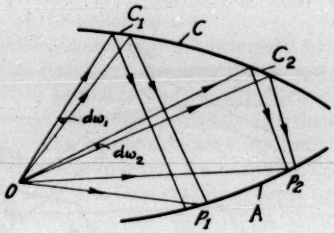
This is the general nature of the proposed solution of the problem. The quantitative aspect of this method will now be considered.

The first step is to determine the relative sound intensity received from the stage at all portions of the audience surfaces of the hall, the ceiling not being in position. This may be done by a process of summation, assuming that the direct unreflected sound from the stage follows the inverse square law with reasonable accuracy, and adding to the intensity of sound at each point calculated in this way the intensity of sound coming by reflection from the walls and floors estimated on the assumption that regular reflection occurs from all extended surfaces, with diminution of intensity depending on the acoustical absorption coefficient of the reflecting material. The varying intensities arrived at by the summation of these two effects are then noted at the corresponding points on the plan of the hall.

The second and final step is to design the form of ceiling, which in conjunction with the reflecting surfaces already considered will produce the desired distribution of sound intensity over the audience surfaces. The nature of the solution may be understood by reference to Fig. 1. p_1 and p_2 are two points on the audience surface A at which the

sound received from the source O by direct transmission and by reflection from the walls and reflecting surfaces previously considered has the values $f(p_1)$ and $f(p_2)$ respectively, determined by the general method described above. Let $d\omega_1$ and $d\omega_2$ be two elementary cones of sound energy originating at O, which after reflection at the ceiling C arrive at p_1 and p_2 and communicate to these points sound intensities $f'(p_1)$ and

FIG. I.

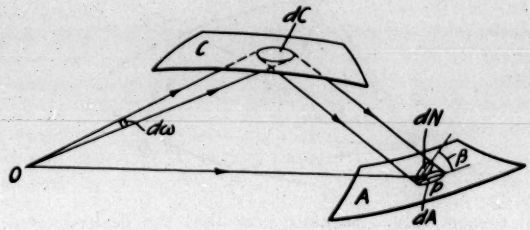


$f'(p_2)$ respectively. Suppose now that the desired total intensities at p_1 and p_2 are $F(p_1)$ and $F(p_2)$, which may or may not be equal. The desired result will be attained provided $f(p_1) + f'(p_1) - F(p_1) = 0$, $f(p_2) + f'(p_2) - F(p_2) = 0$. In these equations $f'(p_1)$ and $f'(p_2)$ are determined, relative to the other quantities, by the values of OC_1, OC_2, C_1p_1, C_2p_2, the curvature of the ceiling at C_1 and C_2, and the absorption coefficient of the ceiling.

Suppose the values of $f(p)$, and $F(p)$ have been reckoned on the assumption that the source O is emitting sound energy at a rate producing unit sound intensity at unit distance from O, and that this assumption is retained throughout the following discussion. And suppose further that an arbitrary unit of rate of flow of sound energy past a surface be adopted such that the source O, on the above assumption is emitting sound energy at the rate of 4π of these units per second. Turning now to Fig. 2 the rate of flow of energy from the source O within the elementary beam of solid angle $d\omega$ is equal to $d\omega$. This beam, impinging on the element dC of the ceiling surface is reflected, and the energy flow along the reflected beam is reduced to $(1 - \mu)d\omega$, where μ is the proportion of the sound energy lost by absorption at dC. dN is

the cross section of this reflected beam at p where it meets the audience surface A and dA is the projection of dN on A. β is the dihedral angle between dN and dA. Simple consideration will show that the intensity of sound at p produced by sound originating at O and subsequently reflected at dC is $(1 - \mu)\frac{d\omega}{dA \cos \beta}$, which is thus the value of the expression $f'(p)$ considered in the previous paragraph. Thus the exact

FIG. 2.



form of the ceiling required to bring about the distribution of sound intensity desired is such that the general equation

$$f(p) + (1 - \mu)\frac{d\omega}{dA \cos \beta} - F(p) = 0$$

must be satisfied throughout the hall.

It is not proposed to enter into a description of the method by which a design of hall in agreement with this equation may be arrived at. If an attempt be made to apply the general formula by direct mathematical methods the labor and time involved in arriving at the required result makes the method impracticable. It will be sufficient to state that a means of dealing with the problem efficiently has been devised, and that the design when completed may be tested readily to determine its effect on sounds originating from points other than that assumed as the source of sound in working out the design.

The form of ceiling arrived at by this method depends on the plan of the theater for which it is designed, and does not closely resemble any simple geometrical form, such as a

figure of revolution. It depends on the height of wall, the nature and form of reflecting surfaces near the assumed source of sound, the form of the audience surfaces, and other factors. It may, however, be stated that in general the longitudinal vertical median section shows increasing curvature towards the back of the hall, and that the transverse vertical sections show the opposite effect. If galleries are present there will be discontinuities in the curvature of the ceiling along certain lines, conforming more or less to the forward edges of the galleries.

The problem of increasing the intensity of sound in deep covered galleries has been studied, but is not dealt with in this paper. It is probable that acoustic conditions in such galleries can never be made perfectly satisfactory, but it is certain that they can be considerably improved.

The method of working out the correct acoustical form of a hall outlined in this article can in general be applied more efficiently to an auditorium than to a theater, since the acoustic conditions in the neighborhood of the stage are far more advantageous in the typical auditorium, and the galleries are in general fewer in number and not crowded forward towards the stage. Certain forms of theater, however, lend themselves very advantageously to this method of treatment. In the case of very large halls the acoustical adjustment of the design must be confined to the rear portions of the hall, since a greater difference of path than 70 ft. (1/15 sec.) between direct and reflected sound will cause duplication effects, which are necessarily disadvantageous. If the vertical walls are made low the reverberation period is bound to be very short with a ceiling designed by the method described, provided the absorption at the audience surfaces is great. It is obvious that very little of the sound originating at the stage will be returned to the stage since the underlying principle of the method is to convey all the available sound to the audience in the shortest possible time, and a very small proportion of sound is reflected by an audience.

Very few theaters and auditoriums are so designed as to provide the same angular clearance for the line of sight of each member of the audience over those seated in front. This result can be attained only by having all the audience

surfaces so formed that vertical sections of these surfaces through the stage conform to the equation $r = e^{a\theta}$. Surfaces formed in this manner have acoustical as well as visual advantages, since diffraction effects at the lower edges of sound waves advancing to the audience directly from the stage are equalized over the entire audience. The double advantage of audience surfaces of this form appears to have been overlooked in most theaters.

The question of phase difference of sound arriving at the audience by different paths is of course extremely important. Serious effects due to interference are not to be expected, however, since there will always be a variety of paths by which sound may travel from the stage to any part of the audience surface, and no serious effects due to selective reënforcement or weakening of definite frequencies are to be anticipated. Such effects are necessarily produced in any auditorium, but are practically never detected. It is not to be anticipated that this difficulty will be noticeably accentuated in the proposed form of hall.

In conclusion it may be said that the type of hall design advocated appears to be the only form which can bring about a logical distribution throughout the audience of sound originating at the stage. It is possible by this method to design an auditorium so that all members of the audience seated beyond approximately two-fifths of the distance to the back of the hall may hear with equal clearness. This applies to short as well as to prolonged tones. It is believed that this result has not been attained in any theater up to the present time.

SOME SECONDARY PHENOMENA IN X-RAY SPECTRA.[1]

BY

F. K. RICHTMYER, Ph.D.,

Professor of Physics, Cornell University.

"History repeats itself."

If you ask the professional historian to explain the meaning of this oft-repeated statement, he will probably tell you that in the evolution and growth of human society he sees the rise and fall of empires; the regular cycle of events—social and economic, as well as military—when peoples engage in wars with each other; or the recurrence of financial panics, with intervening periods of prosperity. If you ask further for a definition of history, you may learn that "history is a systematic record of the past," with particular reference to the interrelations of cause and effect in the development of our social, economic and political institutions.

Now, it is universally recognized that among those factors which are ordering modern society at present, none is more potent than science. Applied science, growing out of the pure science of the laboratory, has, in the hands of various professional groups, completely revolutionized many aspects of present-day life. And yet a very minor place—or, none at all—is given to science either pure or applied in the formal courses in history in our schools and colleges. A recent, popular outline of history gives exactly two and one-half lines to Galileo; to Napoleon, however, many pages. Newton receives a mere passing comment. Benjamin Franklin is lauded as a *statesman*, but there is no mention of his scientific achievements. If The Franklin Institute served no other purpose than by its very existence to keep alive the name and fame of one of the greatest scientists of his time, it would still be doing a very much worth while work.

[1] Based in part on an address delivered before the Institute, Thursday, January 24, 1929.

I do not propose to make a long digression on the history of science. But since we are met under the auspices of an organization which is so rich in historical associations, it may be not inappropriate to give to the evening's discussion an historical background, sufficient at least to point out that a study of the history of science leads to certain broad generalizations applicable, as well, to other phases of man's activities.

Again: "History repeats itself"; but this time let us apply the statement to the history of physics. We go back a little over four decades, to 1887, where we find a very interesting situation. The electromagnetic theory of light, that crowning achievement of nineteenth century physics, reigned supreme, practically unchallenged by either theory or experiment. The work of Hertz in proving experimentally the existence of the electromagnetic waves predicted by Maxwell was the keystone of the arch of triumph of the then "modern" physics. The period was one of extreme confidence in existing physical theories. There seemed some justification for the oft-quoted statement that "henceforth research would be concerned with the next decimal place."

Then came the next phase of the ever-recurring cycle. In rapid succession in the decade following 1887 came the discovery of photoelectricity; X-rays; radioactivity; and the electron. These new phenomena introduced uncertainty, even confusion, into physical theory. "The next decimal place" was partially forgotten in the efforts to make quantitative studies of these new phenomena. Gradually there was evolved the quantum theory, with its varied ramifications. The period of confusion was passing with the accumulation of more data; and again "the next decimal place" began to demand attention. The quantum theory began to crystallize into definite form, to be followed by the present wave mechanics which seems to be, comparatively, as all-embracing as was Maxwell's electromagnetic theory in its time. We of the present are too close to today's events to ascertain our exact position in the cycle. But perhaps in due course the wave-mechanics-quantum theory will become so stabilized and "satisfying" as an explanation of physical phenomena that again "the next decimal place" will assume major proportions. Then, we may look for some new and startling discoveries to usher in a new era and to start another cycle.

These new phenomena, on the basis of which physics makes "quantum jumps" forward, are of two kinds: First, there are the unexpected discoveries such as photoelectricity, X-rays, radioactivity, and the like. Then, there are those other equally important discoveries which result from pushing the precision of measurements as far as possible. From Kepler's discovery of the elliptical motion of the planets, based on a slight difference in the observed and the computed position of the planet Mars, to the discovery of the refraction of X-rays, based on the slight variation in the apparent wave-length of X-rays reflected in different orders, the history of physics is filled with instances of major discoveries resulting from carefully observing the difference between "tweedle dee and tweedle dum." The quantum theory itself arose from just such a small difference between theory and experiment. Let us therefore not speak too slightingly of "the next decimal place." Indeed, it is just this kind of phenomena which are the subject of the present discussion—namely, some of the "little things" in X-ray spectra.

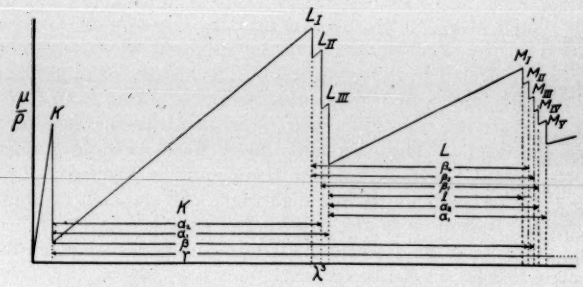
The decade and a half from Röntgen's discovery of X-rays in 1895 until 1910 may be called a period of uncertainty in so far as an understanding of the real nature of X-rays was concerned. Then, as a result of the earlier diffraction experiment of Haga and Wind; of the classical work of Barkla; and of other indirect lines of evidence, it became quite clear that X-rays were like light waves, only of much shorter wave-length. Direct proof of the undulatory nature of X-rays came from the famous Laue-Friedrich-Knipping experiment in 1912 in which it was shown that X-rays may be diffracted from a grating much like ordinary light, and soon thereafter Bragg, Moseley and others showed that, like ordinary light, X-rays comprise both continuous and characteristic, or line, spectra.

Once the true nature of X-rays was understood, the subject developed rapidly so that by, say 1922, a complete scheme of X-ray absorption and emission spectra had been built up. The essential features of this scheme, in so far as concerns the present discussion, are contained diagrammatically in Fig. 1, in which the upper broken line shows the relation (not to

scale) between the mass absorption coefficient[2] μ/ρ of X-rays and the wave-length λ. It is observed that at definite wave-lengths (or frequencies) come sharp breaks in this absorption curve, known respectively as K, L, M . . . absorption limits. There is one K-limit; three L-limits; and so on.

A study of X-ray emission spectra revealed the fact that,

FIG. 1.



Schematic diagram showing relations between X-ray absorption phenomena and line spectra The *frequencies* of the lines (such as $K\alpha_1$, $K\alpha_2$, $L\beta_4$, etc.) are equal to the *differences in frequency* between pairs of absorption limits.

in general, the frequency of a given emission line in the X-ray spectrum is equal to the difference between the frequencies of a particular pair of absorption limits, as is indicated by the arrows in Fig. 1. For example, the frequency of the $K\alpha_1$ line is equal to the difference in frequency between the K-limit and the L_{III}-limit. The $L\alpha_1$ line is equal to the difference in frequency between the L_{III}-limit and the M_V-limit. Thus from a knowledge of the number of possible pairs of limits, the *complete* X-ray line spectrum should be predictable.

By reference to Fig. 1, we may now summarize as follows some of the empirical data of X-ray spectroscopy, as those data were understood, say, a decade ago.

(1) The mass absorption coefficient, μ/ρ, of a given substance for X-rays is a linear function of the cube of the wave-

[2] In the well-known equation for absorption of radiation

$$I = I_0 e^{-(\mu/\rho)\rho x},$$

I is the intensity of a beam of radiation, initial intensity I_0, after passing through a slab of the absorbing material of thickness x and density ρ.

length between adjacent absorption limits. (This is the well-known "cube" law, frequently written in the form:

$$\frac{\mu}{\rho} = k\lambda^3 + \frac{\sigma}{\rho},$$

where the term σ/ρ represents scattering. The law is represented graphically by the straight lines between the absorption limits.)

(2) At certain definite wave-lengths, characteristic of each absorbing substance, are observed discontinuities (the *vertical* lines of the diagram) which seem to be sharp within the limit of error of measurement.

(3) The wave-length (or frequency) at which a given discontinuity for a particular absorbing substance occurs is *independent of the physical or chemical state of the absorber.*

(4) The *complete* X-ray emission spectrum is predictable from the possible combinations of pairs of absorption limits (subject to a selection principle which rules out certain combinations). The general scheme of X-ray spectra, both emission and absorption, seemed simple and complete.

However, with the ever increasing precision with which X-ray measurements have been made in recent years, and with the extension of those measurements to longer and longer wave-lengths, it is now evident that the four statements just made are approximations only, and that X-ray spectral phenomena are much more complicated than was previously assumed. With more accurate data at hand we may now modify, seriatim, the above statements somewhat as follows:

(1′) The λ^3-law of X-ray absorption holds approximately, but there are certain small, though consistent, deviations therefrom.

(2′) The absorption discontinuities are not quite sharp, but show a definite structure.

(3′) The wave-length at which a given absorption discontinuity occurs varies slightly with the chemical combination of the absorber.

(4′) There are numerous *faint* lines in X-ray emission spectra which are *not* predictable by any possible combinations of pairs of absorption limits such as are shown in Fig. 1. (These faint lines are called satellites and are usually found

close to, but on the high frequency side of, the more prominent lines which *do* fit the diagram of Fig. 1, and which, to distinguish from them the satellites, are called "diagram" lines.) We may refer to the physical factors which necessitate the making of the modified statements (1′) to (4′) as "secondary phenomena" in X-ray spectra. By way of illustration we discuss the last two: namely, (3′) the effect of chemical combination on absorption limits, and (4′) X-ray satellites.

X-RAY ABSORPTION LIMITS AND CHEMICAL COMBINATION.

Existing data tend to show that, broadly speaking, both the structure of an absorption limit, and the frequency of the limit depend on the state of chemical combination of the absorber. Data on the structure of absorption limits, however, seem to be somewhat more ambiguous than data on frequency, and we shall therefore confine our discussion to the latter question.

The first to observe a definite dependence of the wavelength of an absorption limit on chemical combination seems to have been Berengren [3] who studied the K-absorption edge of phosphorus. His data for black phosphorus and for phosphorus in phosphoric acid are as follows:

TABLE I.

	λ of K-edge.	Excitation Potential.
Black phosphorus	5.767 A	2140.6 volts
Phosphoric acid	5.750	2147.0

From the Einstein relation

$$Ve = h\nu_K,$$

where V is the potential difference through which electrons must fall to generate radiation of frequency ν_K (e ≡ charge on electron; h ≡ Planck's constant; ν_K ≡ frequency of K absorption limit) one can compute the excitation potentials corresponding respectively to these two edges. It is seen that it requires higher-voltage cathode rays to "knock" K-electrons from phosphorus in phosphoric acid than from black phosphorus; the difference being some 6.4 volts, or 0.3 per cent.

[3] *Zeit. Phys.*, 3, 247, 1920.

Whatever the physical reasons for this difference, the interpretation of the result is perfectly definite: On account of the chemical combination of phosphorus in phosphoric acid, more energy is required to extract a K-electron from it than from free phosphorus.

Following this observation by Berengren numerous investi-

TABLE II.

Wave-length of K-absorption Edge of Phosphorus in Various Chemical Combinations (after Stelling, loc. cit., 1928).

	Compound.	Wave-length of K-edge.	Excitation Potential.	ΔV above White P.
(*a*)	P(white)	5.7769 A.	2137.3 volts	—
	P(black)	5.7715	2139.3	2.0 volts
	P(violet)	5.7714	2139.3	2.0
	$(RO)_3PO$	5.7507	2147.1	9.8
	$(RO)_2HPO$	5.7541	2145.8	8.5
	$(RO)H_2PO$	5.7575	2144.6	7.3
	$(RO)_2(RC)PO$	5.7551	2145.6	8.3
(*b*)	$(RO)(RC)_2PO$	5.7591	2144.0	6.7
	$(RC)_3PO$	5.7604	2143.5	6.2
	$(RC)_4POR$	5.7630	2142.5	5.2
	$(RN)Cl_2PO$	5.7588	2144.1	6.8
	$(RN)(RO)(Cl)PO$	5.7559	2145.2	7.9
	$(RN)(RO)_2PO$	5.7512	2146.9	9.6
	$(RN)_2(RO)PO$	5.7541	2145.8	8.5
	$(RN)_3PO$	5.7565	2145.0	7.7
	$(RO)_3P$	5.7599	2143.7	6.4
(*c*)	$(RC)_3P$	5.7676	2140.8	3.5
	$(RO)Cl_2P$	5.7602	2144.6	7.3

gators [4] studied the effect for the lighter elements—mainly, Si(14), P(15), S(16), Cl(17), K(19), Ca(20), Cr(24) and Fe(26). The early results, although confirming beyond question the observations of Berengren, were somewhat ambiguous, quan-

[4] Some of the more important references to this subject are the following:
Berengren, J., *Zeits. für Phys.*, *3*, 247, 1920; *Comptes Rend.*, *171*, 624, 1920.
Lindh, A. E., *Comptes Rend.*, *172*, 1175, 1921; *175*, 25, 1923. *Zeits. für Phys.*, *6*, 303, 1921; *31*, 210, 1925.
Coster, D., *Zeits. für Phys.*, *25*, 83, 1924.
Chamberlain, K., *Nature*, *114*, 500, 1924; *Phys. Rev.*, *26*, 525, 1925.
Stelling, O., *Zeits. für anorg. Chem.*, *131*, 48, 1923; *Zeits. für phys. Chem.*, *117*, 161–175–194, 1925; *Chem. Ber.*, *60*, 650, 1927; *Zeits. für Phys.*, *50*, 506, 1928; Dissertation, Lund, 1927.
Aoyama, Kimura and Nishina, *Zeits. für Phys.*, *44*, 810, 1927.

titatively. We refer therefore directly to the recent work of Stelling (loc. cit., 1928), and quote therefrom the data on the K-edge of phosphorus in various compounds:

Columns (1) and (2) of Table II are taken directly from Stelling's paper. The first three items are the allotropic modifications of phosphorus. In the remaining items "R" stands for a monovalent element or radical. Section (*b*) of the table contains compounds in which phosphorus is pentavalent; part (*c*) contains three divalent compounds. Stelling found that, for a given type of compound the wave-length of the K-edge is independent of R. Thus $(NaO)_3PO$ gives the same edge as $(KO)_3PO$. The wave-length of the edge does, however, depend in a definite way on the nature of the group, or groups, which combine with "PO" to form the molecule. Thus, replacing one (RO) group in $(RO)_3PO$ by H results in a longer wave-length of the K-edge. Replacing two (RO) groups gives a still longer wave-length. The effect of an (RC) group as compared with an (RO) group is the same for pentavalent as for trivalent sulphur.

The significance of these measurements is made clearer by reference to the third column of Table II in which are tabulated the values of the K-excitation potentials of phosphorus in the several compounds, as computed from the wave-lengths of column (2), according to the well-known formula

$$V = \frac{hc}{e\lambda} = \frac{12345}{\lambda},$$

in which V is given in volts if λ is in Ångstroms. (e, c and h have the meanings usually assigned to them.) It is seen that the K-excitation potential of white phosphorus is lowest; of red and of black phosphorus some two volts higher; and that in compounds considerably higher potentials are required, as is shown in column (4) in which are given the amounts by which the excitation potentials are above that of white phosphorus. Thus the K-excitation potential of phosphorus in $(RO)_3PO$ is 9.8 volts higher than for white phosphorus. These excitations potentials are shown graphically in Fig. 2. Why these differences?

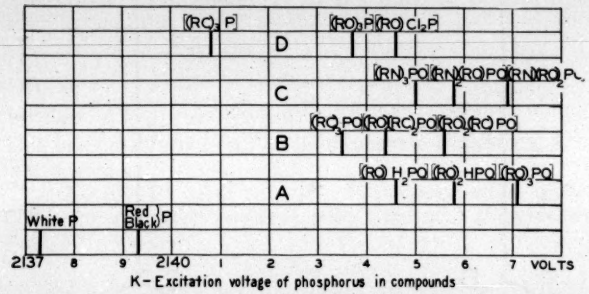
The answer to this question is rather fundamental. The atomic number of phosphorus is 15. According to accepted

theory, phosphorus has two K-, eight L- and five M-electrons. In phosphates, such as $(RO)_3PO$, the five M-electrons are taken up by the surrounding atomic groups, as represented by the structural formula:

$$\begin{array}{c} (RO) \\ | \\ (RO) - P = O. \\ | \\ (RO) \end{array}$$

The phosphorus atom is thus left with only K- and L-electrons. If, now, we assume that electrostatic forces of attraction be-

FIG. 2.

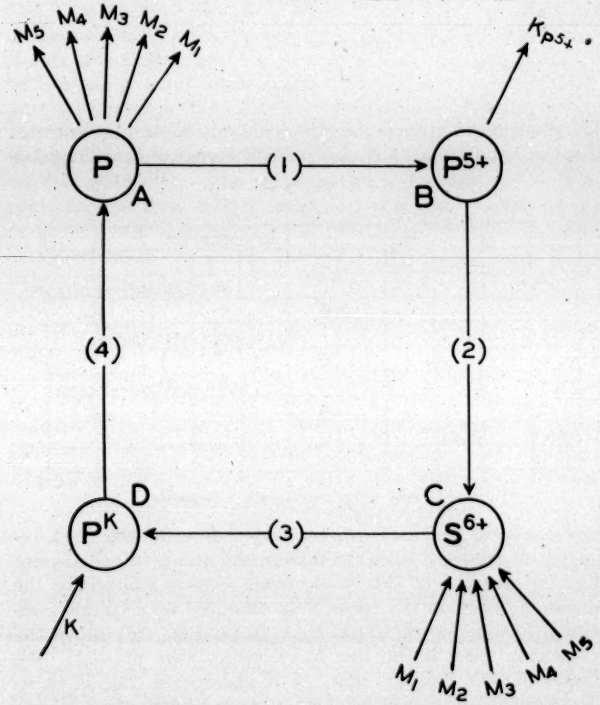


tween nucleus and electron are responsible for the work required to remove a K-electron from the atom, we see at once that the absence of the M-electrons reduces materially the screening effect on the (positively charged) nucleus and consequently more work would have to be done to remove the K-electron than if the five M-electrons were present. We should therefore expect that the K-absorption edge in phosphates would be found at shorter wave-lengths than in free phosphorus,—which is actually observed to be the case. The magnitude of this difference can be approximately predicted from theoretical considerations by a cyclic process, given by Aoyama, Kimura and Nishina (loc. cit.), in which the P atom is carried through the following cycle:

1. We start with the neutral P atom at *A* (Fig. 3) and re-

move in turn each of the five M-electrons. The total work thereby required is readily estimated from the several ionization potentials of phosphorus, tabulated in Table III. It

FIG. 3.



requires 10.3 electron-volts to remove the first electron; 20.3 electron-volts to remove the second; and so on. The total work required to move all five electrons is proportional to the sum of the five ionization potentials, which sum we may represent by

$$\sum_{1}^{v} I_P.$$

At the end of this process we have a five-fold ionized P atom, symbolically represented by P^{5+} at *B*.

2. We now remove a K-electron from this ionized P atom, a process requiring work which we may represent by

$$K_{P^{5+}}.$$

The removal of this K-electron, in effect, increases the nuclear charge by unity, at least so far as concerns the exterior of the atom. This P atom, which has lost its five M-electrons and one K-electron, is therefore very nearly like a sulphur atom (atomic number 16) which has lost six M-electrons. We may designate it by "S^{6+}" at *C*.

3. To this "S^{6+}" atom we now add, one by one, the five M-electrons. The energy given out may be computed by summing up the *second* to the *sixth* (inclusive) ionization potentials of sulphur; that is

$$\sum_{II}^{VI} I_S.$$

This process results in a P atom minus one K-electron, P^K as represented at *D*.

4. To this P^K atom we add a K-electron, which process brings the atom back to the starting point at *A* and gives out energy

$$K_P.$$

Since the total amount of energy given out by the atom during the cycle must be equal to that expended, we may write

$$\sum_{I}^{V} I_P + K_{P^{5+}} = \sum_{II}^{VI} I_S + K_P.$$

Or

$$K_{P^{5+}} - K_P = \sum_{II}^{VI} I_S - \sum_{I}^{V} I_P.$$

The first term on the left-hand side of this equation represents the work required to remove a K-electron from a P atom which has lost its five M-electrons—exactly as we suppose the P atom in $(RO)_3PO$ to have done. The second term is the work required to remove the K-electron from the normal free P atom. The difference between these two quantities, ex-

pressed in electron-volts, gives the amount by which the ionization potential of P in $(RO)_3PO$ should exceed that of free P. We see that this difference is easily determinable in terms of

TABLE III.

*Ionization Potentials of Phosphorus and Sulphur.**

	P	S	P	S
	in volts.		in ν/R units.	
I.....	10.3	10.3	0.761	.761
II.....	20.3	21.8†	1.50	1.61†
III.....	30.0	34.0†	2.21	2.51†
IV.....	49.3†	47.0	3.64†	3.47
V.....	64.8	69.5†	4.78	5.12†
VI.....		88.0		6.48

* See Aoyama, Kimura and Nishina for references.
† Estimated by interpolation.

the summations shown on the right, which we may easily evaluate from the data in Table III. We find

$$K_{P^{5+}} - K_P = 85.6 \text{ electron-volts.}$$

Owing to the approximations involved, this result may be in error by several, perhaps many, per cent., but it cannot be several fold too large or too small.

However, from Table II we see that the difference between the K ionization potentials of free P (white) and of P in $(RO)_3PO$ is only 9.8 volts—a difference *much* smaller than that predicted on the assumption that all the five M-electrons are removed from the P atom in the process of forming $(RO)_3PO$. The inference, therefore, is that this assumption is incorrect; or at least that so far as electrostatic fields and screening effects go, the RO groups and the O atom play much the same rôle as the M-electrons, the screening effect of the RO group being less, but only a little less, than that of an M-electron. There is a small difference in the screening effect of different groups. (Compare RO, RC and RN.)

It seems probable that investigations of this kind will open up a new avenue of approach to the question of valency and chemical combination. If so, there will be one more justifica-

tion for research "in the next decimal place," since the data contained in Table II are made possible only by pushing the measurements almost to the limits of precision.

SATELLITES OF X-RAY LINES.

As stated above, the diagram lines—that is, the lines the frequencies of which are obtained by taking the differences in frequency between pairs of absorption limits (see Fig. 1)—are the more prominent lines in the X-ray spectrum. In addition to these diagram lines, there are found numerous fainter lines located, usually, close to and on the short wave-length side of the diagram lines. These faint lines have been designated in various ways. They have been called : (1) "non-diagram" lines, since they do not "fit" into the schematic diagrams of Fig. 1, that is, the frequencies of these lines are not simply related to the frequencies of absorption limits; (2) "spark lines," since one theory suggests that their origin is similar to the origin of spark lines in the optical part of the spectrum; (3) "second order lines," since various theories attribute their origin to an initial state of *double* ionization in the atom, just as the diagram lines (sometimes called "first order" lines) originate in *singly* ionized atoms; or (4) "satellites," a term which, in view of the present uncertainty as to their real origin seems more appropriate since it means only that on X-ray spectrum plates these lines are found close to the more intense diagram lines, the origin of which is supposed to be known.

Satellites were first observed by Siegbahn and Stenstrom [5] in their studies of the wave-lengths of the K-series of the elements Na(11) to Zn(30), In the spectrogram for Zn a faint line was observed close to, and on the short wave-length side of, the Kα doublet. For elements of lower atomic number this line becomes more prominent and in the neighborhood of Ca(20) splits up into two lines, apparently a doublet, which are called Kα_3 and Kα_4. Since 1916 numerous investigators [6]

[5] *Phys. Zeit.*, *17*, 48, 1916; *17*, 318, 1916.

[6] Among these may be mentioned the following:

"Spectra of X-rays and the Theory of Atomic Structure," D. Coster, *Phil. Mag.*, *43*, 1070, 1922.

"Das Röntgenspektrum des mehrfach ionizierten Molybdäns," Siegbahn and Larsson, *Arkiv för Matematik och Fysik*, *13*, 1, 1924.

have reported data on satellite lines. Several theories of their origin have been proposed. It is now known that many, but probably not all, of the diagram lines are accompanied by satellites, and that the satellite structure associated with diagram lines varies from line to line.

As typical, may be mentioned the satellites of the $K\alpha$ doublet. The satellite structure accompanying this doublet is known from Na(11) to Zn(30), and is shown diagrammatically in Fig. 4, in which the frequency differences in ν/R units ($\nu \equiv$ frequency in sec.$^{-1}$; R $\equiv$ Rydberg's constant) between the $K\alpha_1$ line and the several satellites are shown for the several elements. The line on the left represents the line $K\alpha_1$. Taking Na(11) as an example it is observed that there are five satellites called respectively α', α_3, α_4, α_5 and α_6, the height of the lines being a very rough qualitative indication of relative intensity. The line $K\alpha'$ has been followed as far as Cl(19). The doublet α_5, α_6 has been observed as far as S(16). The stronger doublet, α_3, α_4 has been observed as far as Zn(30) but has not been resolved above Ca(20). A faint satellite $K\alpha''$ has been observed for several elements. We shall discuss below, the satellites of some of the more prominent L diagram lines. For the present we shall pause to review briefly Wentzel's theory of the origin of the $K\alpha$ satellites, and the various objections to this theory.

According to Wentzel's theory, satellites are produced by *single*-electron jumps between multiply-ionized states. Consider, for example, the satellites of the diagram doublet, $K\alpha_{1,2}$ which originates in atoms which have lost one K-electron.

"Notiz über die Erregung der sogenannten Funkenlinien in der K-Reiche der Röntgenspektren und der Theorie von Wentzel," E. Bäcklin, *Zeits. für Ph.*, *27*, 30, 1924.

"Funkienlinien im Röntgenspektrum," G. Wentzel, *Ann. der Ph.*, *66*, 437, 1921.

"Über die Komplexstruktur der Röntgenfunkenspektren," G. Wentzel, *Zeits. für Ph.*, *31*, 445, 1925.

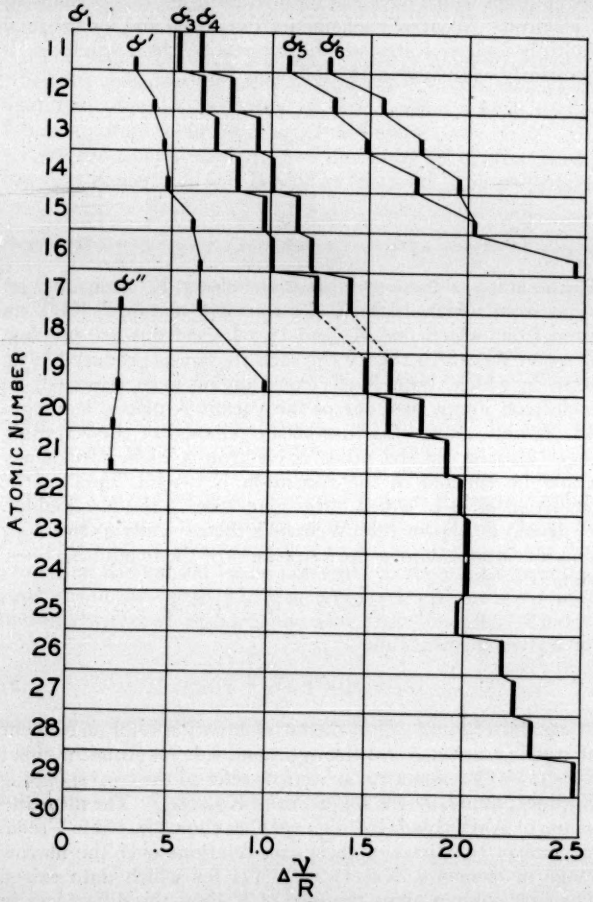
"The Energies of the Multiple Ionization of Light Atoms," L. A. Turner, *Phys. Rev.*, *26*, 143, 1925.

"Über die Funkenlinien des K-Spektrum von Natrium, Magnesium und Aluminum," T. Wetterblad, *Zeits. für Ph.*, *42*, 611, 1927.

"Das Röntgenspektrum zweiter Art," M. J. Dwyvesteyn, *Zeits. für Ph.*, *43*, 767, 1927.

"Het Röntgenspectrum von de tweede Soort," M. J. Druyvesteyn, Dissertation, Groningen, 1928.

FIG. 4.



Satellites of the Kα doublet.

Wentzel (loc. cit., 1921) assumed that the Kα satellites originate in atoms which have lost both K-electrons, and perhaps an L electron. Wentzel's scheme for the initial and for the final multiply-ionized states which give rise to these satellites, is frequently expressed in the following form:

TABLE IV

Satellite.	Initial State.	Final State.
$K\alpha_4$	K^{II}	KL
$K\alpha_3$	KL	L^{II}
$K\alpha_6$	$K^{II}L$	KL^{II}
$K\alpha_5$	KL^{II}	L^{III}
$K\alpha'$	KM	LM

The meaning of these symbols is as follows: K^{II} designates an atom from which both K-electrons are missing; KL^{II}, an atom from which one K- and two L-electrons are missing. Thus on Wentzel's theory the satellite $K\alpha_4$ is produced in an atom in which, both K-electrons having been removed, an L-electron jumps into one of the vacant K-places, leaving a KL ionized atom. Because of the removal of the screening effect exerted by the other K-electron a higher frequency would be emitted in the transition $K^{II} \rightarrow KL$ than in the transition $K \rightarrow L$, which latter gives rise to the Kα doublet.

It can be shown that Wentzel's theory leads to two very simple relations among the frequencies of the several Kα lines, viz:

$$\nu_3 - \nu_1 = \nu_5 - \nu_3 = \nu_6 - \nu_4 \qquad (1)$$

for a given element; and

$$(\nu_6 - \nu_4)_Z = (\nu_3 - \nu_1)_{Z+1}, \qquad (2)$$

where the lefthand side of the latter equation is for an element of atomic number Z and the righthand side for atomic number $Z + 1$. (The numerical subscripts refer to the corresponding Kα lines; thus $\nu_3 \equiv$ the frequency of $K\alpha_3$, etc.) The measurements of Wetterblad (loc. cit., 1927) as shown in Table V seem to confirm the latter of these two relations over the narrow range of elements, Na(11) to Si(14) for which data exists. The first column gives the pair of K lines the differences in frequency between which in ν/R units for the several elements

are shown in the other columns. Relation (1) of Wentzel's theory is not verified, but the data seem to indicate substantial agreement with relation (2).

The difficulty with Wentzel's theory, however, appears when one considers the possible sequence of events which may lead to a double ionization of the K shell. Such double ionization may occur in either of two ways:

(1) An atom in the target of the X-ray tube, after having lost one K-electron and before an electron from an outside

TABLE V.

Frequency Difference—in ν/R Units—between Pairs of $K\alpha$ Lines for the Elements Na(11) to Si(14).

	Na(11)	Mg(12)	Al(13)	Si(14)
$\Delta(\alpha_3 - \alpha_1)$	0.52	0.64	0.71	0.83
$\Delta(\alpha_5 - \alpha_3)$	0.57	0.67	0.76	0.91
$\Delta(\alpha_6 - \alpha_4)$	0.65	0.76	0.83	0.94

orbit falls into the vacant K place, may be struck by a second cathode ray electron under such conditions as may result in expelling the second K-electron. A simple computation, however shows that this "tandem" process, though possible, cannot account for satellites as intense as those observed. For, the relative intensity of a satellite, say $K\alpha_4$, and the diagram line $K\alpha_1$ should be proportional to the relative number of atoms in the target which at any given instant are doubly and singly ionized, respectively, as to their K-shells. That is,

$$\frac{I_{\alpha_4}}{I_{\alpha_1}} = \frac{N^{IIK}}{N^{IK}},$$

when N^{IK} and N^{IIK} stand, respectively, for the number of singly- and doubly-ionized atoms, and I_{α_4} and I_{α_1} are the intensities of the lines α_4 and α_1. Now, if N represents the total number of atoms in the target which at one time or another take part in producing X-rays, then

$$\frac{N^{IK}}{N}$$

is known to be a very small fracton, the value of which is

determined, for a given target, partly by the "life" of atoms in the IK ionized state and partly by the number of cathode ray electrons which, per second, strike the target. If we assume that the probability that an atom of a given kind shall be "struck" by a cathode-ray electron is proportional to the number of such atoms present in the target, then it follows that the probability of IIK ionization must be very small in proportion to the probability of IK ionization, and that the relative intensity of the satellite $K\alpha_4$ must be correspondingly small compared to the intensity of $K\alpha_1$. The observed intensity, however, of $K\alpha_4$ is many fold greater—indeed of a different order of magnitude—than could be predicted on this tandem-process theory, by making any reasonable assumptions as to the value of the fraction N^{IK}/N.

Further, on this theory of the process of double ionization of the K-shell, we should expect that the intensity of $K\alpha_4$ should increase proportionally to the *square* of the cathode-ray current in the X-ray tube; that is, the relative intensity of satellite to diagram line should increase with increase in absolute intensity of the diagram line. This is readily seen to follow. For, using the above symbols

$$I_{\alpha_4} \propto N^{IIK} \propto N^{IK} \times n_e,$$

where n_e is the number of cathode-ray electrons per second striking the target. But ^{IK} is proportional to n_e. Therefore

$$I_{\alpha_4} \propto n_e^2.$$

However, there seems to be no experimental evidence to indicate that there is a change of relative intensity of satellites and "parent" line with change of current through the X-ray tube.

(2) We may visualize another process for double ionization of the K-shell. It is thinkable—at least so far as energy relations go—that a single cathode-ray electron possessing sufficient kinetic energy, may, by colliding with an atom, cause the expulsion of both K-electrons. Since the energy required to remove the second K-electron must be somewhat greater than that required to remove the first, it follows that the excitation potential of $K\alpha_4$ should be somewhat more than twice as great as that of $K\alpha_1$.

Precise measurements of the excitation potentials of satellites are lacking, but such data as exist indicate clearly that the excitation potentials of $K\alpha_{3,4}$ are *less* than twice the excitation potentials of $K\alpha_{1,2}$. Bäklin (loc. cit.), for example, found that the $K\alpha_{3,4}$ of Al(13) is produced at 2.9 KV, while the excitation potential of $K\alpha_{1,2}$ is 1.55 KV. Druyvesteyn (loc. cit.) finds that $K\alpha_{3,4}$ of Va(23) is produced at 6.45 ± 0.1 KV, the excitation potential of $K\alpha_{1,2}$ being 5.45 KV.

It seems therefore that the theory that double ionization of the K-shell as the initial state in the production of $K\alpha_{3,4}$ must be abandoned.

Druyvestyn (loc. cit., 1927), however, presents experimental evidence which seems to show that some, at least, of the satellite lines can be explained by the double-ionization theory discussed above, provided that in no case is it assumed that the initial state, in the production of a given line, involves double ionization in the *same* shell.

Druyvestyn's method may be illustrated by discussing his explanation of the origin of the line $K\beta'''$, which is a satellite of the diagram line $K\beta$ and which has been measured over the range of elements Al(13) to Fe(26). $K\beta'''$ is resolved into a doublet for Al(13), Si(14) and P(15). Druyvestyn assumes that this line is due to the transition

$$KL \rightarrow LM,$$

whereas the $K\beta$ line is due to the transition

$$K \rightarrow M.$$

It is possible to make an approximate estimate of the frequency to be expected for a quantum emitted by the transition $KL \rightarrow LM$: Let $(E_{KL})_Z$ be the energy of an atom of atomic number Z from which a K- and an L-electron have been removed; $(E_L)_{Z+1}$ the corresponding energy of an atom of atomic number $Z + 1$ from which an L-electron has been removed; etc. Then

$$h\nu_{K\beta'''} = (E_{KL})_Z - (E_{LM})_Z.$$

Now, to a close approximation

$$(E_{KL})_Z = (E_K)_Z + (E_L)_{Z+1}$$

and

$$(E_{LM})_Z = (E_L)_Z + (E_M)_{Z+1},$$

since, in $(E_{KL})_Z$ for example, the removal of the K-electron leaves the atom, so far as concerns the removal of the L-electron, very much like an atom of atomic number Z + 1. Remembering that

$$h\nu_{K\beta} = (E_K)_Z - (E_M)_Z,$$

we have

$$(h\nu_{K\beta'''} - h\nu_{K\beta})_Z = [(E_L)_{Z+1} - (E_L)_Z] - [(E_M)_{Z+1} - (E_M)_Z].$$

The left hand side of this equation is proportional to the difference in frequency between the satellite $K\beta'''$ and the parent line $K\beta$ for an element of atomic number Z. From the right hand side we see that this frequency difference is computable from the known L and M energy levels of atoms of atomic numbers Z and Z + 1, respectively.

Table VI, quoted from Druyvesteyn (loc. cit., 1928) shows the comparison of the observed, with the computed frequency differences, in ν/R units.

TABLE VI.

Comparison of Observed and Computed Frequency Difference between the Satellite $K\beta'''$ and the Parent Line $K\beta$, in ν/R units.

Element.	Observed.		Computed.	
			$L_{II, III}$.	L_I.
Al 13.....	1.79	2.23	1.82	2.34
Si 14.....	2.07	2.74	2.11	2.63
P 15.....	2.38	2.97	2.40	2.92
S 16.....	2.97		2.70	3.22
Cl 17.....	3.27		2.97	3.49
K 19.....	3.59		3.55	4.07
Ca 20.....	3.83		3.84	4.36
Sc 21.....	3.77		3.53	4.05
Ti 22.....	3.72		3.73	4.25
V 23.....	3.92		3.95	4.47
Cr 24.....	4.00		4.16	4.68
Wn 25.....	4.34		4.38	4.90
Fe 26.....	4.69		4.58	5.10

The column headed "$L_{II, III}$" is computed from the above equation by assuming the mean of the energy levels L_{II} and L_{III}; and similarly for the column headed L_I. It is observed that the agreement between observed and computed values is good, particularly for those elements for which $K\beta'''$ is resolved.

Applying the above scheme, Druyvesteyn proposes the following transitions, Table VII, as the origin of the several K- and L-satellites:

TABLE VII.

Druyvestyn's Proposals of the Origin of Satellites.†

Parent Line.	Satellite.	Initial State.	Final State.
$K\alpha$	$K\alpha'$	KL_{2_1}	$L_{2_1}L_{2_2}$
	$K\alpha_{3,4}$	KL_{2_2}	$L_{2_2}L_{2_2}$
	$K\alpha_{5,6}$	$KL_{2_2}L_{2_2}$	$L_{2_2}L_{2_2}L_{2_2}$
*$K\beta$	$K\beta'''$	KL_{2_1}	$L_{2_1}L_{2_2}$
		KL_{2_2}	$L_{2_2}L_{2_2}$
$L\alpha$	$L\alpha'$ to $L\alpha^{IV}$	$L_{2_2}M$	MM_{3_2}
$L\beta_1$	$L\beta_1'$ and $L\beta_1''$	$L_{2_2}M$	MM_{3_2}
*$L\beta_2$	$L\beta_2'$ and $L\beta_2''$	$L_{2_2}M$	MN_{4_2}
*$L\gamma_1$	$L\gamma_1'$	$L_{2_2}M$	MN_{4_2}
*$L\gamma_{2,3}$	$L\gamma_{2,3}'$	$L_{2_1}M$	MN_{4_2}

† The terminology for representing the ionized states is obvious; for example "$L_{2_1}L_{2_2}$" represents an atom from which an L_{2_1} and an L_{2_2} electron are missing; $L_{2_2}L_{2_2}$, an atom from which two L_{2_2} electrons are missing; etc.

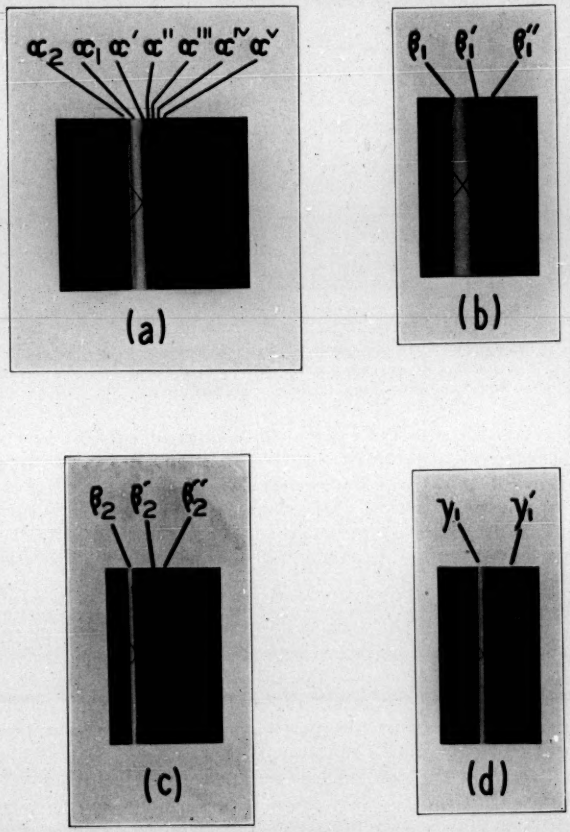
Druyvesteyn presents experimental data in support of the suggested origin of the satellites of parent lines marked with an asterisk (*), but for perhaps a majority of cases, the agreement between the observed and computed values of frequency difference can hardly be regarded as more than qualitative. He shows no data to confirm the suggested origin of the satellites of $K\alpha$ and of $L\alpha$, which groups are the most prominent of all the satellites.

In view of the difficulties with Wentzel's theory, and of the incompleteness of the evidence in support of Druyvesteyn's hypothesis, it may not be inappropriate to suggest an alternative theory of the origin of satellites. Before so doing, however, it is pertinent to present a summary of certain data obtained by the author and others.

Recently, the author had an opportunity in Professor Siegbahn's laboratory [7] at Upsala, Sweden, to make a series of spectrum plates, with the special purpose of bringing out satellite structure, for some of the more prominent L lines in

[7] The author wishes to take this occasion to thank Professor Siegbahn and his colleagues for the many courtesies extended during this investigation.

FIG. 5.

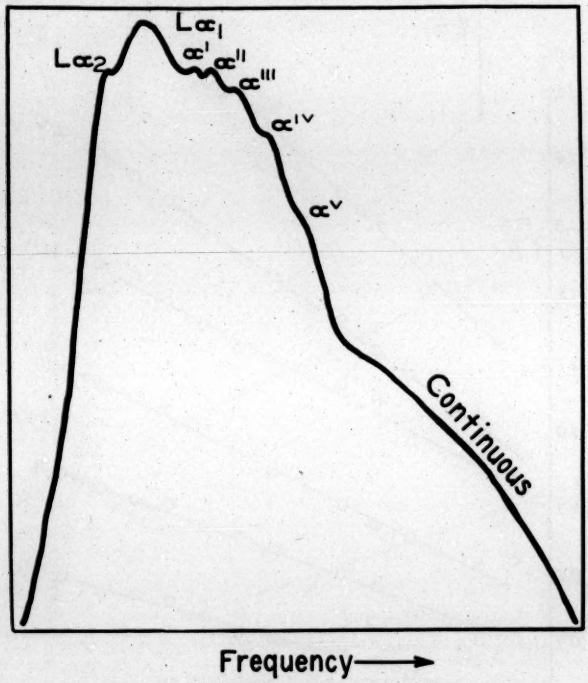


Reproductions of spectrum plates showing satellites of some of the L lines.
(*a*) $L\alpha$ of Ag(47)
(*b*) $L\beta_1$ of Mo(42)
(*c*) $L\beta_2$ of Ag(47)
(*d*) $L\gamma_1$ of Ag(47)

the atomic number range Rb(37) to Sn(50). A careful study [8] of these plates shows that satellites are somewhat more numerous than has been heretofore assumed.

Fig. 5 (*a*) is a reproduction of one of the spectrum plate

FIG. 6.



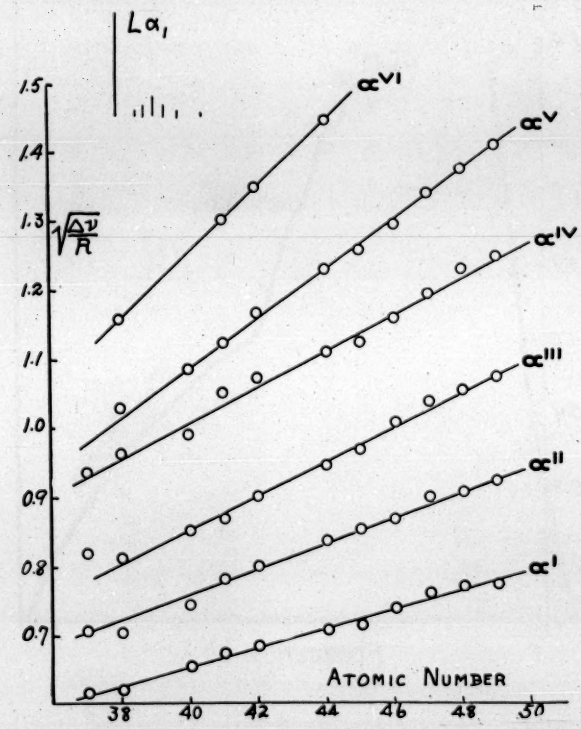
Densitometer curve of the Lα doublet of Ag(47) showing the satellite structure.

showing the satellite structure of the Lα doublet for Ag(47). On the original plate five satellites are easily seen. On some

[8] For the opportunity of making these plates, and for assistance in studying them, the author is indebted to the Heckscher Research Council of Cornell University for a grant in aid of this research; and to his son, R. D. Richtmyer, who cooperated in making the plates.

of the plates, particularly for elements of lower atomic number, two additional faint lines may be observed. Beginning with the one next to $L\alpha_1$, we may designate these satellites respectively, as $L\alpha'$, $L\alpha''$, $L\alpha'''$, $L\alpha^{iv}$ . . . $L\alpha'$ is weak; $L\alpha''$

FIG. 7.



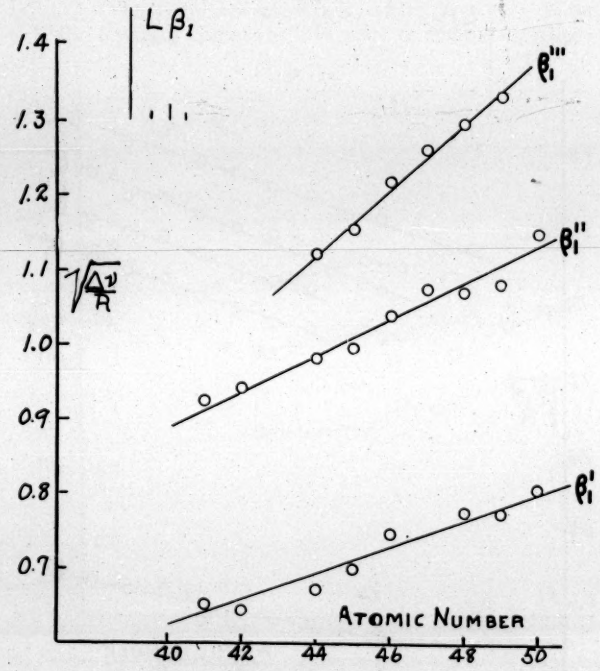
The "Moseley graph" for the satellites of Lα, showing the linear relation between $\sqrt{\Delta\nu}$ and atomic number for six of the satellites.

and $L\alpha'''$ are much stronger, perhaps of equal intensity, and have the appearance of a doublet. Beginning with $L\alpha^{iv}$, they

become rapidly fainter, so that $L\alpha^{vi}$ and $L\alpha^{vii}$ are observed only on plates which have had long exposures.[9]

Fig. 6 shows a densitometer record of the $L\alpha$ doublet of Ag(47) with its satellite structure. The first five satellites are

FIG. 8.



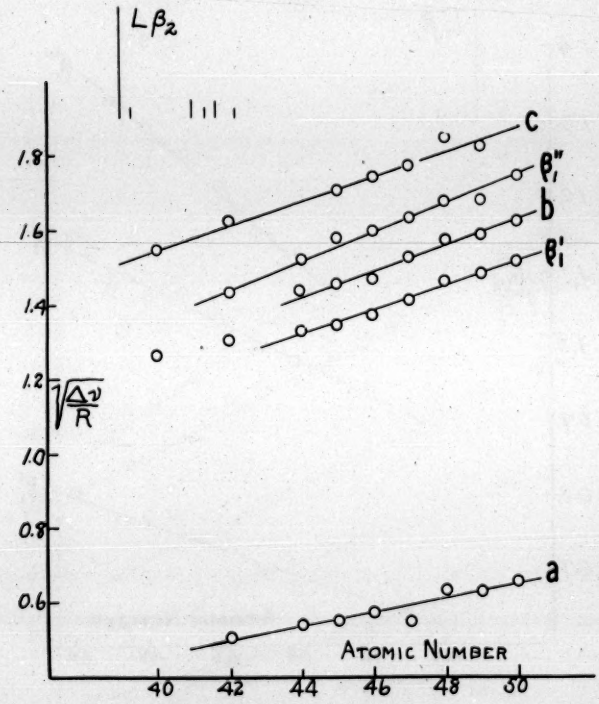
The "Moseley graph" for the satellites of $L\beta_1$.

clearly observed. Extending from $L\alpha^v$ for a considerable distance toward shorter wave-length *there seems to be a rather faint continuous spectrum.* A similar continuous spectrum has

[9] Siegbahn and Larsson (*Arkiv. för Matematik, Astronomy och Fysik, 18,* 1, 1924) report five satellites, $L\alpha'$ to $L\alpha^v$ inclusive, for Mo(42), and suggest that there is, possibly, a sixth $L\alpha^{vi}$.

been observed on so many of the plates, that one seems justified in making the tentative statement, to be tested by further experiment, that many, if not all, of the satellites of X-ray lines are accompanied by a short continuous spectrum not

FIG. 9.



The "Moseley graph" for the satellites of $L\beta_2$.

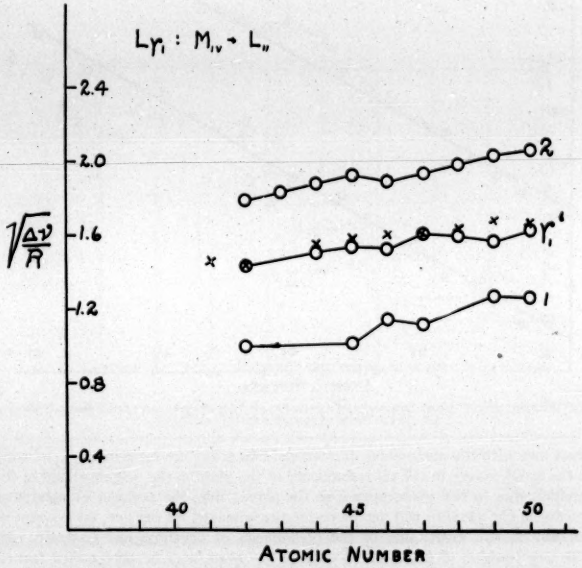
unlike that which one finds beyond the series limit of, say, the Balmer series of hydrogen.

The writer has shown [10] that the frequencies of the $K\alpha$ satellites, $K\alpha_3$ and $K\alpha_4$, are simply related to the frequencies of

[10] *Phil. Mag.*, *6*, 64, 1928.

the "parent" line: Let ν_S and ν_P represent, respectively, the frequency of a satellite and of the parent line. Then the graph of $\sqrt{\nu_S - \nu_P}$ as a function of atomic number N is a straight line—a kind of Moseley graph. Fig. 7 shows such a graph for six of the satellite of $L\alpha$ for the elements Rb(37) to In(49). (The ordinates are $\sqrt{\Delta\nu/R}$, where $\Delta\nu \equiv \nu_S - \nu_P$ and R is the Rydberg constant.) In spite of some scattering of

FIG. 10.



The "Moseley graph" for the satellites of $L\gamma_1$. (The crosses are from data by Druyvesteyn, loc. cit.)

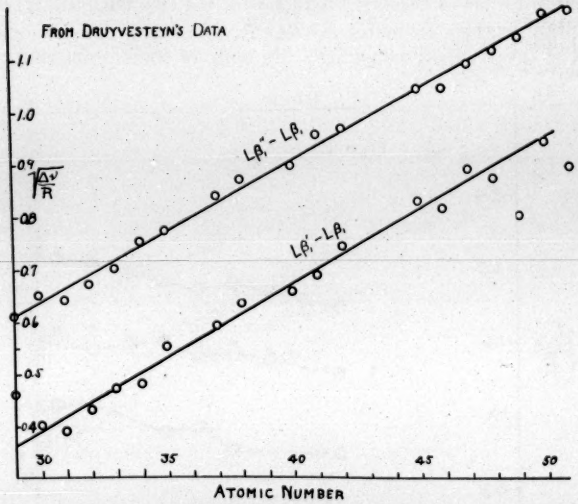
the points, due in part to the difficulty of making precise observations [11] of the wave-lengths of satellites one seems

[11] This difficulty arises from the fact that the satellites in general lie very close to the parent line. In order to bring out the satellite structure, one must make such long exposures that the parent line is much overexposed, with the result that the satellites lie "in the shadow" of the latter. In measuring the plates in the

justified in concluding that $\sqrt{\Delta\nu}$ is a linear function of atomic number N.

This same law holds for satellites of other lines. Fig. 5*b*,

FIG. 11.



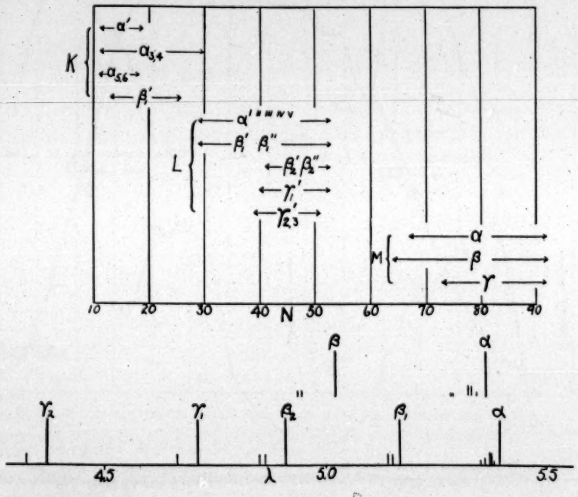
The "Moseley graph" (from Druyvesteyn's data, loc. cit.) for the two more prominent satellites of $L\beta_1$ for the range of elements Cu(29) to Sn(50).

usual way with the micrometer microscope, two errors are introduced: (1) Owing to the rapid change in the general density of the plate in the neighborhood of the satellite, due to the overexposure of the parent line, the position of maximum density in the satellite will not be correctly estimated by the eye, on account of the well known errors due to the phenomena of psychological contrast. (2) The true position of maximum *density* on the plate may be determined from a densitometer record such as Fig. 6, but this does not give the true position of maximum *intensity* of the satellite, since, as above noted, the actual plate density in the neighborhood of the satellite is the sum of densities produced separately by the satellite and parent line. Only if we know the *slope* of the density curve of the *parent* line in the neighborhood of the satellite can we, from the *correct* position of observed maximum density of the plate, compute the *correct* position of maximum intensity of the satellite. It is difficult, *if not actually impossible*, to determine this slope. Hence the values of $\Delta\nu$ in curves 7 to 10 are obtained directly from the *uncorrected* readings with a micrometer microscope. Errors of a few per cent., varying perhaps from line to line, are thereby introduced.

c, *d* are reproductions of spectrum plates showing satellites of $L\beta_1$, $L\beta_2$ and $L\gamma_1$. Figs. 8, 9 and 10 show the corresponding graphs of $\sqrt{\Delta\nu/R}$ against N. In each case, the linear relation previously mentioned, is observed to hold. Indeed, Druyvesteyn (loc. cit., 1928) has extended the measurements on the satellites $L\beta_1'$ and $L\beta_1''$ from Sn(50) down to Cu(29). Fig. 11 shows the Moseley-type of graph for his data, in complete agreement with the above.

In passing, mention may be made of the fact that five

FIG. 12.

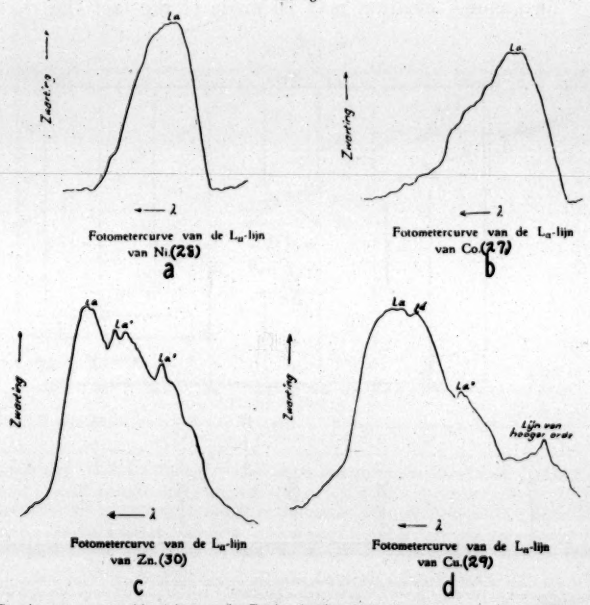


The lower part of the figure shows, on a wave-length scale, five of the diagram lines of Mo(42), viz: $L\alpha$, $L\beta_1$, $L\beta_2$, $L\gamma_1$ and $L\gamma_2$, with their respective satellites. Immediately above are two K lines of S(16), namely $K\alpha$ and $K\beta$, with their satellites. The upper part of the figure shows the range of atomic numbers over which the respective satellites are found.

satellites are shown for $L\beta_2$, of which, so far as the writer knows only two have been reported previously, namely those called by Druyvesteyn $L\beta_2'$ and $L\beta_2''$ (Siegbahn: $L\beta_{11}$ and $L\beta_{12}$) respectively. These two are the strongest of the five. The remaining three have been designated, temporarily, on Fig. 9

as "a," "b" and "c," in lieu of a systematic terminology for satellites. Satellite **a** lies very close to $L\beta_2$ and unless very carefully observed appears merely as a slight broadening of $L\beta_2$ toward short wave-lengths. Satellites **b** and **c** are very faint and diffuse. Indeed it is difficult to say with certainty whether they are real lines or whether they are part of the faint continuous spectrum which, as previously mentioned, seems

FIG. 13.



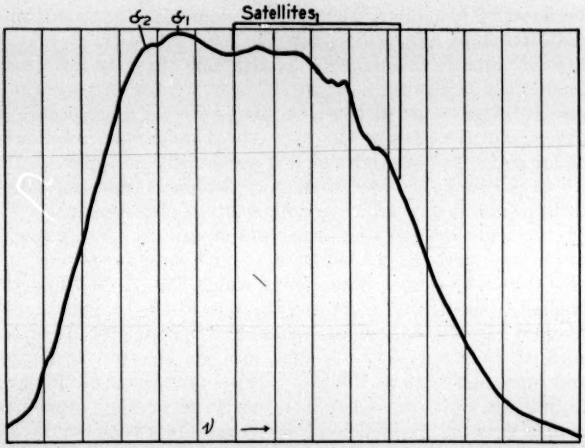
Densitometer curves of Lα (after van der Tuuk), showing the sudden appearance of Lα satellites at Cu(29) and Zn(30).

to accompany satellites. This point can be decided only after much further careful study.

It is very significant that satellites of a given parent line are not observed over the entire range of elements for which the parent line is observed. This fact is brought out in Fig. 12.

At the bottom of the figure, plotted to a wave-length scale (Ängstroms), are five of the more prominent L-series lines of Mo(42), viz. α, β_1, β_2, γ_1 and γ_2, together with some of the satellites of each shown by the shorter lines. The two lines α and β, in the next row above, are to the same wave-length scale, the Kα and Kβ lines of S(16), with their satellites. The upper part of Fig. 12 shows the range of atomic numbers over

FIG. 14.



Densitometer curve of Lα of Mo(42), showing the prominence of the satellite structure.

which each of the satellites has been observed. The most prominent of the K-satellites, namely K$\alpha_{3,4}$, are found over the range Na(11) to Zn(30) inclusive. At least two of the satellites of Lα (i.e., the two more prominent ones) have been measured from Cu(29) to the neighborhood of Sn(50). In general, we may say that K-satellites are found from Na(11) to Cu(29); L-satellites, from Cu(29) to Sn(50); and M-satellites from about atomic number 65 or 70 to U(92).

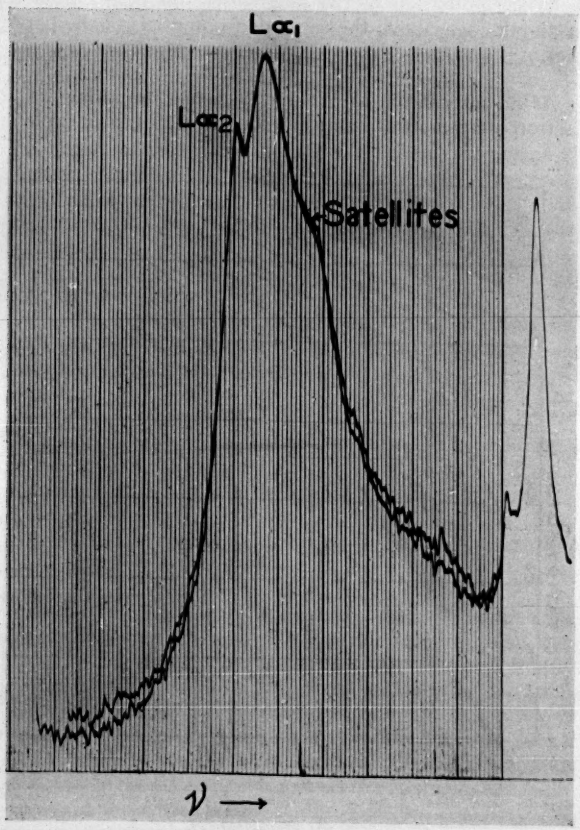
Satellites seem to disappear rather abruptly as one passes outside the range of atomic numbers for which each satellite has been observed. The satellites L$\alpha^{iii, iv}$ may be taken as

examples. Fig. 13 shows a series of densitometer curves for the line Lα as observed by van der Tuuk (loc. cit., 1928), for the elements Co(27) to Zn(30). No satellites are observed (on the short-wave-length side of the curves) for Co(27) and Ni(28). But beginning with Cu(29) distinct satellite structure is found, and this is so well developed at Zn(30), that the five satellites are readily observable. Proceeding toward higher atomic numbers, the relative intensity of the satellite structure seems to increase, perhaps reaching a maximum in the neighborhood of Mo(42) as shown by a densitometer record of a plate taken by the author, Fig. 14. At Cd(48) the five satellites are readily distinguishable, although they are less prominent than in Mo(42). At In(49) they are not well separated and at Sn(50) a broad band, showing little or no structure, is observable as shown in Fig. 15. This band has been followed as far as Ba(56) beyond which it apparently disappears.

It is probably more than a coincidence that, according to the Bohr theory of the arrangement of electrons in K-, L-, M- . . . groups, the above ranges of atomic numbers, namely, 11–29 and 29–50, over which K- and L-satellites occur, are also the approximate ranges over which the M-shell and the N-shell, respectively, increase from one to 18 electrons. The M-shell has one electron at Na(11) and is complete at Cu(29) with 18 electrons. The N-shell has one electron at Zn(30) and increases to 18 at Pd(46). This coincidence would seem to indicate that the K-satellites are in some way connected with a growing M-shell; and the L-satellites with a growing N-shell. We shall refer to this point later.

Concerning the excitation potentials of satellites in general, only very meagre qualitative data are to be found. There are collected in Fig. 16 such data as seem to have a bearing on the present discussion. The excitation potential of the K-series of Va(23) is 5.45 K.V. Druyvesteyn (loc. cit., 1928) has shown that the satellite $K\alpha_{3,4}$ is not produced at potentials under 6.09 ± 0.1 K.V., and that $K\beta'''$ is produced at potentials below 6.44 K.V. Siegbahn and Larsson (loc. cit.) found that the excitation potential of the first four satellites of Lα of Mo(42) lies between 3.0 and 4.0 K.V., while the excitation potential of Lα itself (initial state, L_{III} ionization) is 2.52 K.V. Similar data, from Druyvesteyn, are shown for

FIG. 15.



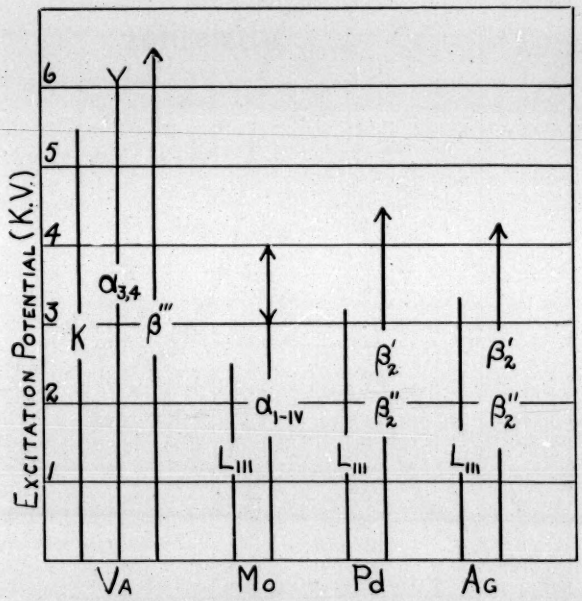
Densitometer curve of Lα of Sn(50), showing that the satellite structure is much less prominent than with Mo(42).

the $L\beta_2$ satellites of Pd(46) and Ag(47), the excitation potentials being less than 4.5 and 4.3 K.V., respectively. The excitation potentials of the L-satellites, therefore, are some 20–30 per cent. above the excitation potentials of the parent lines.

TWO-ELECTRON JUMPS.

As an alternative to Wentzel's theory proposing *single*-electron jumps between multiply-ionized states as an explana-

FIG. 16.



Excitation potentials of satellites for several elements in comparison with the excitation potentials of the "parent" lines. Actual excitation potentials of satellites are not known. Rather, the figure shows limiting potentials above which (upward pointing arrow) the satellites are found, or below which (downward pointing arrow) they are not found.

tion of the origin of satellites, let us consider the possibility that these lines may originate in *two*-electron jumps between multiply-ionized states. Let us assume that as a result of an

ionization process an atom has become doubly ionized, having lost an electron from one of its inner shells—K or L, call it an "*i*" shell—and from one of its outer shells, call it an "*o*" shell. Then let an electron from, say, the next shell outside the *i* shell drop into the vacant place in the *i* shell, emitting thereby a quantum of energy, frequency ν_i, given by

$$h\nu_i.$$

This quantum would correspond very closely to one of the diagram lines since the absence of an outer-shell electron has only a small effect on inner-shell phenomena. Next, let a valence electron drop into the vacant place in the "*o*" shell, a quantum

$$h\nu_o$$

being thereby emitted.

Now, it is possible that both of these "jumps" might occur simultaneously and as a result there might be emitted a *single* quantum of frequency ν_S given by

$$h\nu_S = h\nu_i + h\nu_o.$$

The spectral line of frequency ν_S would then be a *satellite* of the *parent* line of frequency ν_i.

In support of this suggestion may be advanced the following arguments:

1. From the preceding equation we obtain the following:

$$\sqrt{\nu_S - \nu_i} = \sqrt{\nu_o}.$$

Since ν_o is the frequency of a spectral line, we might expect Moseley's law to apply to it, and accordingly $\sqrt{\nu_o}$, and therefore $\sqrt{\nu_S - \nu_i}$, should be a linear function of atomic number N — *at least over the range of elements within which the number of electrons in shell o is increasing regularly.* As pointed out above, K-satellites are known only over the range of elements for which the M-shell is being filled; and L-satellites occur approximately over the range for which the N-shell is being filled. Figs. 7–10 show that for the L-satellites this linear relation is observed; and a similar relation has been found [12] for the K-satellites.

2. It might be expected that occasionally a free electron,

[12] F. K. Richtmyer, *Phil. Mag.*, *6*, 64, 1928.

possessing kinetic energy $\frac{1}{2}mv^2$, might approach the atom under such conditions that it would drop into the vacant place in the *o* shell, simultaneously with the transition which fills the *i* shell and as a result a quantum of energy (i.e. a "satellite")

$$h\nu_S = h\nu_i + h\nu_o + \tfrac{1}{2}mv^2$$

might be emitted. In the totality of such events in the target of the X-ray tube free electrons possessing a range of kinetic energies might unite with atoms, and hence we should have a continuous spectrum as part of the satellite structure. As mentioned above, such a faint continuous spectrum is frequently observed, and would perhaps always be found with proper exposure. It extends some 50 to 60 volts beyond the satellites. Partially spent cathode-ray electrons possessing kinetic energy of 50–60 electron-volts are almost certainly present in the target, at least in thick targets. It would, however, be interesting to ascertain whether this continuous spectrum would be found in satellite spectra from very thin targets, in which very few, or none at all, cathode-ray electrons of low velocity should be present.

3. The differences in frequencies between satellites, whether K-, L- or M-, and their respective parent lines *all fall within the approximate range* 0.8 to 4.0 in ν/R units. This may be observed from an inspection of the ordinate scales of Figs. 7–10, and of the corresponding diagram for Kα satellites.[13] According to the proposed two-electron-jump theory, this *frequency difference* should be the *frequency* ν_o of the quantum which would be emitted by the outer-electron jump should it occur alone. It is to be expected that ν_o/R would fall within the range of values of the first several ionization potentials of the various elements. From Table III, we see that the first five ionization potentials of P(15) and S(16) are included within the approximate range 0.8 to 5.0 in ν/R units. The third ionization potentials of Zn(30) [14] and of Sn(50) [15] are, respectively 2.96 and 2.22. However, existing data on ionization potentials and on spectral phenomena of the peripheral parts

[13] Loc. cit., *Phil. Mag.*, *6*, 64, 1929.
[14] Laport and Lang, *Phys. Rev.*, *30*, 378, 1927.
[15] Green and Loring, *Phys. Rev.*, *30*, 574, 1927.

of the atom are too meager to warrant more than qualitative inferences from this point.

4. From the data recorded graphically in Fig. 16, it appears that the excitation potentials of the satellites are some 20–30 per cent. higher than those of the corresponding parent line. This excess is somewhat higher than would be expected for simultaneous ionization of the *i* (inner) and *o* (outer) shell on the theory proposed. However, it must be remembered that the data on the excitation potentials of satellites is limited, and is difficult to get. Preliminary (unpublished) data taken by the writer indicates that satellites may be produced at voltages somewhat lower than has been heretofore supposed.

However, existing data concerning X-ray satellites are comparatively limited. The evidence in support of the above suggestion of two-electron jumps is hardly more than circumstantial. Before this suggestion can be raised to the dignity of a theory much more data must be obtained. In any event, here, as in other branches of physics, a study of "little things," or with somewhat more dignity "secondary phenomena," seems to promise important results.

CORNELL UNIVERSITY,
June 10, 1929.

Sixty Years Ago. *The Engineer*, London, August 9, 1929. In the late 'sixties we gave much attention to the merits and demerits of various types of breech-loading rifles. Invention in that direction was at the time very prolific. It would be a mistake to suppose, however, that even as late as 1869 no one could be found to support the muzzle-loader, in spite of all that had been done and said about the breech-loader. At any rate, it would appear from a note in our issue of August 6th, 1869, that there were still some who required the evidence of a direct test to convince them of the superiority of the newer type of weapon. A convincing trial was afforded them. A squad of fifteen picked men armed with long Enfield muzzle-loading rifles was placed in competition against three men armed with Soper direct-action breech-loaders. Each party was to fire as rapidly as they pleased for three minutes at 200 yards. The muzzle-loaders made a total score of 272. The three breech-loaders scored a total of 388. One of the breech-loaders got off 56 shots in the three minutes. Another actually scored five bull's-eyes before a single shot was fired by any of the fifteen muzzle loaders. . . . In the same issue Professor Macquorn Rankine began a discussion of "The Dynamical Principles of the Motion of Velocipedes." It was intended to be an elementary explanation of why a two-wheeled machine could be balanced, steered and propelled, a subject on which much curiosity and much ignorance then prevailed. The dynamical principles were correctly expounded, as was to be expected of the author. It is, however, doubtful if he really succeeded in making the explanation clear to many of his readers. It was based on the general principle that the motion of the common center of mass of a set of bodies cannot be altered by the mutual action of those bodies. That principle is not among the stock of knowledge possessed by the average person even to-day. How, then, could it be expected to provide a convincing demonstration of the motion of a bicycle at a time when, even among engineers, dynamical knowledge was so confused that force, power, *vis viva* and energy were used by many to represent the same thing, when even the simple distinction between stress and strain was, for most, a matter of great difficulty to understand?

THE ABSORPTION SPECTRUM OF BROMINE VAPOR BETWEEN 6117 Å. AND 6309 Å.

BY

MARGARET B. HAYS, M.S.

IT has been observed by many investigators [1, 2, 3] that when the radiation from a continuous source is passed through a layer of bromine vapor, a few centimeters thick, the wave-lengths below 2500 Å. are absorbed, while there is complete transmission between 2500 Å. and 3400 Å. approximately. For thicker layers, a wide absorption band begins about 3400 Å. and extends to the yellow region and when the layer is very thick the absorption continues into the red. Beyond 5100 Å. depending on the thickness of the vapor used, there appears a banded spectrum which at ordinary temperatures has been observed to extend as far as 6800 Å.

This banded spectrum has been studied by Hasselberg,[4] Narayan and Gunnayya,[5] Nakamura,[6] and Kuhn.[7] The wave-lengths of the lines making up the bands between 5159 Å. and 6162 Å., have been measured by Hasselberg. Nakamura with layers varying in thickness from 2 cm. to 120 cm. measured only the band edges or heads which he arranged into series using formulæ of the Deslandre type. Kuhn has also measured the edges of the bands and arranged them into two dimensional series by means of the "length" and "cross" differences. On the whole the agreement between Kuhn and Nakamura observations is fair although most of Kuhn's values are larger, in some cases as much as 3 Å.

The object of this investigation was to extend the measure-

[1] Kayser, Handbuch der Spectroscopie, Bd. III, p. 320.
[2] Bovis, *Ann. de Phys.*, 10, 232 (1928).
[3] Ribaud, *Ann. de Phys.*, 12, 165 (1919).
[4] Hasselberg, *Vet. Ak. Handl. Stockholm*, 24, 1 (1890–91).
[5] Narayan and Gunnayya, *Phil. Mag.*, 45, 827 (1923).
[6] Nakamura, *Mem. Coll. Sci. Tokio Imp. Univ.*, 9, 335 (1926).
[7] Kuhn, *Zeit. f. Physik*, 39, 77 (1926).

ments of the wave-lengths of the lines constituting these bands beyond those given by Hasselberg, and to study the relation of the lines to the band heads in the light of modern theory.

TABLE I

$n_1 = 3, n_2 = 6$		$n_1 = 4, n_2 = 8$		$n_1 = 3, n_2 = 5$	
λ	ν	λ	ν	λ	ν
6117.49	16342.06	6141.17	16279.05	6166.36	16212.54
6119.04	16337.92	6142.33	16275.97	6167.43	16209.78
6120.56	16333.86	6143.45	16273.00	6168.60	16206.66
6121.23	16332.08	6144.60	16269.95	6169.77	16203.58
6121.69	16330.85	6145.66	16267.16	6170.32	16202.14
6122.16	16329.59	6146.77	16264.22	6171.86	16198.10
6122.67	16328.24	6147.98	16261.02	6173.28	16194.37
6123.15	16326.95	6149.11	16258.03	6174.20	16191.96
6123.67	16325.56	N6150.18	16255.20	6175.04	16189.75
6124.20	16324.16	6150.90	16253.30	6176.56	16185.77
6124.89	16322.31	6151.59	16251.47	6177.82	16182.47
6125.44	16320.85	6152.55	16248.93	6178.75	16180.04
6126.05	16319.33	6153.84	16245.53	6179.48	16178.12
6126.67	16317.57	6154.10	16244.84	6180.19	16176.26
6127.13	16316.35	6154.57	16243.60	6180.95	16174.28
6128.11	16313.74	6155.28	16241.73	6181.85	16171.92
6129.82	16309.19	6155.84	16240.25	6182.75	16169.57
6131.23	16305.44	6156.29	16239.06	6183.48	16167.66
6131.86	16303.76	6156.94	16237.35	6184.36	16165.36
6132.40	16302.33	6157.66	16235.45	6185.20	16163.16
6132.83	16301.19	6158.50	16233.24	6186.12	16160.76
6133.57	16299.22	6158.95	16232.08	6187.00	16158.46
6134.05	16297.93	6159.55	16230.44		
6134.55	16296.61	6160.20	16228.60		
6135.30	16294.62	6161.52	16225.28		
6135.94	16292.92	6162.28	16223.28		
6136.63	16291.09	6163.18	16220.91		
6137.48	16288.83	6164.41	16217.67		
6138.44	16286.29	6165.15	16215.73		
6139.38	16283.79				
6140.34	16281.25				

EXPERIMENTAL METHODS.

The source of continuous radiation was a 65 watt lamp with a short, straight, helical filament. It was surrounded by a hood with a hole in its side. The light passing through this hole was made parallel by a lens and then allowed to pass through a layer of bromine vapor 80 cm. in thickness. The tube containing the vapor had plane glass windows fastened on with glue and the junctions covered with paraffin. A few cc. of C.P. bromine were introduced and allowed to vaporize

and completely fill the tube before closing. There was always some liquid present so the gas was at the vapor pressure for room temperature. The light was then focused on the slit of a fourteen-foot concave Rowland grating which had a dispersion of 3.639 Å. per mm. in the first order. The spectrum was photographed on Wratten and Wainwright panchromatic plates with a time of exposure varying from three to six hours.

$n_1 = 4, n_2 = 7$		$n_1 = 3, n_2 = 4$		$n_1 = 4, n_2 = 6$	
λ	ν	λ	ν	λ	ν
6187.90	16156.11	6218.46	16076.71	6236.98	16028.97
6188.93	16153.42	6219.66	16073.61	6237.81	16026.84
6189.92	16150.94	6221.08	16069.94	6238.77	16024.38
6190.85	16148.41	6222.48	16066.33	6239.67	16022.07
6191.40	16146.98	6223.18	16064.52	6240.64	16019.57
6191.91	16145.65	6223.64	16063.33	6241.54	16017.26
6192.99	16142.83	6224.15	16062.02	6242.43	15014.98
6194.00	16140.20	6224.60	16060.86	6243.46	16012.34
6195.09	16137.36	6225.12	16059.51	6244.53	16009.60
6196.07	16134.81	6225.66	16058.12	6245.61	16006.83
6196.62	16133.38	6226.18	16056.78	6246.47	16004.63
6197.22	16131.81	6226.81	16055.16	6247.64	16001.63
6197.83	16130.23	6227.33	16053.81	6248.69	15998.94
6198.47	16128.56	6228.00	16052.09	6249.48	15996.92
N6199.49	16125.92	6228.67	16050.36	6249.99	15995.61
6200.60	16123.02	6229.29	16048.66	6250.62	15994.00
6201.28	16121.25	6229.99	16046.96	6251.28	15992.31
6201.96	16119.48	6230.69	16045.16	6251.78	15991.03
6202.93	16117.12	6231.33	16043.51	6252.30	15989.80
6203.59	16115.25	6232.09	16041.55	6252.58	15988.99
6204.40	16113.15	6232.84	16039.62	6252.99	15987.94
6205.51	16110.26	6233.66	16037.52	6253.57	15986.46
6206.40	16107.95	6234.41	16035.58	6253.90	15985.61
6207.22	16105.83	6235.29	16033.32	6254.35	15984.46
6208.45	16102.63	6236.08	16031.29	6254.78	15983.33
N6209.83	16099.06			6255.20	15982.29
6211.07	16095.84			6255.69	15981.04
6212.10	16093.17			6256.17	15979.81
6213.51	16089.52			6256.70	15978.46
6215.24	16085.04			6257.16	15977.28
6216.56	16081.63			6257.66	15976.01
				6258.08	15974.93

An iron arc was used to obtain the comparison spectrum. Screens were employed to prevent all the light except that transmitted by the bromine from falling on the slit of the grating.

Later when the spectrum was photographed in the second

order of the grating where the intensity is greatly reduced, a 30 cm. absorbing layer replaced the 80 cm. one previously employed. A Wratten red stained gelatine filter was used to cut out the possible fourth order of the continuous spectrum

$n_1 = 5, n_2 = 4$		$n_1 = 3, n_2 = 3$		$n_1 = 4, n_2 = 5$	
λ	ν	λ	ν	λ	ν
6258.60	15973.61	6271.97	15939.56	6289.50	15895.13
6259.05	15972.45	6272.57	15938.03	6290.31	15893.08
6259.68	15970.85	6273.13	15936.61	6291.10	15891.09
6260.06	15969.88	6273.81	15934.88	6291.89	15889.09
6260.57	15968.58	6274.46	15933.23	6292.20	15888.31
6261.07	15967.31	6275.14	15931.50	6292.67	15887.12
6261.51	15966.18	6275.78	15929.88	6293.08	15886.08
6262.06	15964.78	6276.40	15928.30	6293.51	15885.05
6262.59	15963.43	6277.08	15926.58	6294.01	15883.74
6263.08	15962.18	6277.71	15924.98	6294.50	15882.50
6263.69	15960.63	6278.37	15923.31	6294.98	15881.29
6264.18	15959.38	6279.00	16921.71	6295.51	15879.95
6264.69	15958.08	6279.70	15919.93	6296.04	15878.62
6265.27	15956.60	6280.41	15918.13	6296.70	15876.95
6265.84	15955.15	6281.13	15916.31	6297.28	15875.49
6266.40	15953.72	6281.84	15914.51	6297.91	15873.95
6266.96	15952.30	6282.44	15912.99	6298.46	15872.52
6267.54	15950.82	6283.15	15911.19	6299.17	15870.73
6268.07	15949.47	6283.79	15909.57	6299.86	15868.99
6268.67	15947.95	6284.47	15907.85	6300.56	15867.23
6269.01	15947.08	6285.21	15905.98	6301.30	15865.36
6269.44	15945.98	6285.99	15904.00	6302.18	15863.15
6270.05	15944.42	6286.64	15902.36	6302.75	15861.71
6270.67	15942.86	6287.43	15900.36	6303.57	15859.65
6271.27	15941.34	6288.12	15898.62	6304.43	15857.49
		6288.75	15897.03	6305.27	15855.37
				6306.15	15853.16
				6306.96	15851.12
				6307.91	15848.74
				6308.88	15846.30
				6309.73	15844.17

N These heads agree with Nakamura but were not observed by Kuhn so no quantum numbers were assigned.

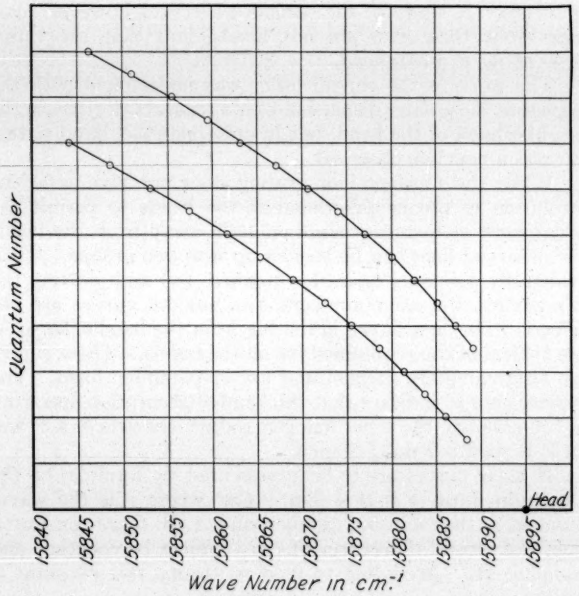
between 2500 Å. and 3400 Å. The wave-lengths were determined by means of a Gaertner comparator reading to 0.001 mm.

DISCUSSION OF RESULTS.

For the region 6117 Å. to 6309 Å., measurements of the wave-lengths of the lines on the four plates taken in the first order were made. The four measurements of each line were

averaged, the maximum variation from the mean being ±0.4 Å. The wave-lengths which were observed in the region 6117 Å to 6237 Å. on the plate taken in the second order agree, within the limits of experimental error, with the average values for the lines in this region. In the first order the lines between 6117 Å. and 6122.3 Å. as well as between 6126.7 Å. and 6131.1 Å. were too faint to measure, so the wave-lengths

FIG. 1.



in the second order are given in the table for these two intervals. These wave-length values with the wave-numbers in cm.$^{-1}$ reduced to vacuum as obtained from Kayser's "Tabelle der Schwingungszahlen" are given in the table above. Following Kuhn, n_1 is the initial quantum number and n_2 the final quantum number assigned to the band head. In the

table, the first number in a column is the wave-length of the head of the band.

Twelve heads have been measured and found to agree within experimental error with those given by Nakamura. Kuhn observed only nine heads in the same region, of which all but two have greater wave-lengths than those of Nakamura. However two of the heads 6199.9 Å. and 6210.7 Å. as given by Nakamura are very doubtful. These appear to be heads but this may be due to the overlapping of the lines of the different branches. A study of the second differences however, indicates that these two are not heads, and that the third, 6150.18 Å., is a real head.

The work in the second order was undertaken with the hope that the greater dispersion would separate the lines in the neighborhood of the head, but in only one case, band 6218.5 Å., was a new line observed.

While the fourteen-foot grating does not give sufficient resolution in the neighborhood of the heads to permit the assignment of quantum numbers, still away from the heads the observed lines can be broken up into two groups. Then arbitrarily assigning quantum numbers (m) and plotting the m's against the wave-numbers, two smooth curves are obtained. The ones shown in the Fig. 1 for the band 6289.50 Å. are typical of those obtained for all the bands. These curves are approximately parallel and are of parabolic form. The curves seem to indicate that the banded absorption spectrum of bromine like the other halogen, iodine, consists of a P and an R branch but no Q branch.

If these curves are to be represented by formulæ of the Deslandre type, $\nu = A + Bm + Cm^2$ where ν is the wave-number, m the quantum number, and A, B, C are constants, then the second differences of the ν's must be constant and equal to $2C$. According to modern theory this constant C equals

$$\frac{h}{8\pi^2 c}\left[\frac{1}{I'} - \frac{1}{I}\right]$$

where I' is the initial moment of inertia, I the final, h Planck's constant, and c the velocity of light. Kemble and Witmer's [8]

[8] Kemble and Witmer, *Phys. Rev.*, 28, 633 (1926).

analysis of the banded absorption spectrum of iodine gave a value for C equal to -0.01. The average of all the second differences for each branch of all the bands given in the table gives C equal to -0.05, which is, within experimental error, of the same order as that for iodine.

Finally, I should like to express my appreciation to Dr. James Barnes, at whose suggestion this problem was undertaken, for his continued encouragement and advice throughout the progress of the investigation. To Dr. E. E. Witmer of the University of Pennsylvania I am indebted for his kind suggestions on the band analysis.

Bryn Mawr College,
Bryn Mawr, Pa.,
May, 1929.

Rubber in Whale Fishery. *India Rubber World*, August 1, 1929. The formation of a German whaling company calls attention to whale fishing and the production of whale oil. There are two whaling ships in the harbor of Hamburg at present, where the whale blubber is worked into oil. The whales that have been caught are brought alongside these boats and are kept afloat by means of air that is pumped into them with the help of long rubber tubes measuring about 30 meters in length and having an inside diameter of 25 mm. On the whale, which may weigh 200 tons, stand the men who cut up the body into convenient sections that are conveyed to the deck of the ship by means of a rubber belt 1,500 mm. wide and 15 mm. thick. When the oil has been extracted, it is led into tanks through rubber tubes 10 m. long. The waste is worked into fish meal, and for carting this material a number of electric carts or barrows are used which are furnished with suitably protected tires to prevent slipping on the greasy decks.

That whaling is still an active industry may be judged from the fact that within four months of this year no fewer than 1,400 whales were caught, and some 40,000 casks of whale oil, each containing 1,000 kilos of oil, were produced.

R.

Nitrogen Fixation. *Commerce Reports*, August 19, 1929. The nitrogen-fixation industry in Japan originated in 1908, when a small hydroelectric plant was built at Sogi, Kyushu, for the manufacture of cyanamide under the Frank Caro process. Actual production began in the plant in 1909, and in 1911 Mr. Fujiyama, one of the principals of this company, discovered a process less expensive than the Caro process. His invention was registered and a new company, the Nihon Chisso Kabushiki Kaisha, was formed. The Mitsubishi interests are large holders in this concern, which has steadily developed and is now the largest single producer of ammonium sulphate in Japan, production during 1928 having reached 100,000 tons. The rights of the Casale process for nitrogen fixation were acquired by this firm and that process is now used in their two mills at Mizumata and Nobeoka, Miyasaki Prefecture, Kyushu. This company has under construction a hydro-electric plant in Chosen, which will shortly be completed. This plant is to manufacture ammonium sulphate, the estimated annual production to be 100,000 tons. Another plant, which will be located in Chosen, is also planned and will have an annual capacity of 200,000 tons.

R.

THE THEORY OF RECOMBINATION OF GASEOUS IONS.

BY

LEONARD B. LOEB

AND

LAURISTON C. MARSHALL.

Physical Laboratory, University of California.

ABSTRACT.

The bearing of the recent results of Marshall on the theory of recombination of gaseous ions is discussed. It is shown, by solution of the Brownian movement equation for two ions of opposite sign, in a gas, that the average relative displacement in a time τ is little influenced by the attractive forces, except for distances of the order of magnitude of 10^{-5} cm. or less, at ordinary temperatures. This conclusion, that in general the motion of the ions relative to each other is largely one of random diffusion, is in good agreement with the interpretation forced by Marshall's study of the variation of the coefficient of recombination α with time and concentration of ions. This also indicates that the theoretical approach of Langevin to the solution of the recombination problem is untenable, while that of Thomson is justified. The theory, of Thomson is discussed and, is compared with observation. It appears to fit qualitatively as accurately as the facts are known. It is then shown how the success of any theoretical treatment is limited due to our ignorance of the nature of the mass of the ion, a condition which, however, enables us to understand the very small range of variation of α among the different gases.

In his book on the Kinetic Theory of Gases, Loeb [1] has dealt at some length with the theory of the mechanism of the recombination of gaseous ions. In this discussion, it is seen that the understanding of this process is far from satisfactory. Later attempts at improvement have also proved futile and it became obvious that no understanding of the phenomenon could be arrived at until new experimental facts bearing on the following problems should be available.

1. The question as to whether the fundamental mechanism of recombination is one of the chance encounter of oppositely charged ions moving in a gas with their random heat motions and very little influenced by the attractive forces (viewpoint of J. J. Thomson),[2] or whether the recombination is due to a

drifting together of the ions with velocities due to the mobilities of the ions in the fields produced by the ionic charges (theory of Langevin [3]).

2. If, in case the Thomson viewpoint were correct, the effect of the charges on the ions, at closer encounter, could be such as to make the Richardson-Thomson correction factor ϵ, determining the probability of recombination in close encounter, incorrect, a possibility first suggested by Cravath.[1]

3. Whether the electron generated in the ionizing process, which is free from considerable intervals of time, as known today, influences the value of the coefficient of recombination observed for ions and how. Assumed evidence in this direction had been obtained by Rümelin [4] who observed very high values of the coefficient over short time intervals in measurement.

4. Whether it is possible to find an explanation for the fact that the value of the coefficient of recombination observed in most gases is nearly the same, in spite of the wide difference in the mobilities and diffusion coefficients as well as the supposed velocities of heat agitation of the ions in the various gases.

5. Finally, an investigation of the nature of the equation used for evaluating the coefficient of recombination from experiment, in view of the unknown initial distribution of ions after ionization (partially columnar distribution and partly distribution in pairs) makes it very doubtful whether the value of the coefficient, deduced from experiment, is even quantitatively correctly evaluated. This suspicion was later found to be partly substantiated by the results of Plimpton,[5] which were, however, made under the earlier conditions, where the complete control of variables was impossible and no important conclusions could be drawn.

Using a new direct method not possible at the time when the earlier work was done Marshall [6] has obtained results which are being published elsewhere, but which may be summarized as follows:

1. The coefficient of recombination, α, was found to be variable, depending on the ionization or flash period of the X-rays used, t', on the time over which the recombination was measured, t, and on the initial density of ions, n_0.

a. The shorter t' and t the higher the value of α.

b. α dropped from values of the order of 4×10^{-6}, for time intervals $t' + t$ of the order of 0.0016 seconds, to a nearly constant value of 1.2×10^{-6} for values of $t' + t$ of .0125 seconds. The effect as regards t' also involves the effect to be discussed under *d*.

c. Thereafter α appeared to approach a constant value of between 0.8 and 0.9×10^{-6} which may be taken to represent the true value of α. Values of all earlier workers are high due to the effects to be mentioned in explaining *a*, *b*, *c*, and *d*, or the inclusion of loss of ions by diffusion which was not adequately corrected for.

d. α is lower the higher the value of the initial concentration n_0 of the ions, being abnormally high for low concentrations.

2. These results are in general in agreement with the initial high values observed by Rümelin [4] and Plimpton,[5] which, however, could not show the effect of varying n_0, t, or t', separately. The explanation given by Plimpton is along the proper lines. His study definitely shows that the high values of α are due to the initial non random distribution of the ions in space, following ionization, in that the ions are (*a*) initially generated in pairs relatively close together, and (*b*) the pairs are distributed along the paths of the photo-electrons generating them, i.e., to some extent columnar. As time goes on, the ions tend to drift apart attaining a practically random distribution in some 0.03 seconds. The accurate evaluation of α requires a chamber of different design from that used in order to obtain higher precision. At present the absolute value of α can only be taken as being good to 10 per cent.

3. Since the theory of Langevin would lead one to expect a nearly constant value of α, these results, together with the obvious interpretation, indicate conclusively that, in general, the tendency of the ions is to drift apart. The forces, therefore, play a secondary rôle in the process of recombination as regards the time element. Thus the ions may be assumed to come together largely as a result of their heat motions.

4. The recombination coefficient α in *pure* argon was measured. In argon one might expect a value of α about

that in air. The observed value was closely *constant* over all times in argon and low, being slightly *less* than the final values in air. Addition of enough oxygen to cause the electrons to attach to form ions in argon and prevent rapid electron diffusion, in the shortest time intervals measured (i.e. the elimination of the free electrons present in pure argon by means of small amounts of oxygen), lead at once to values of α varying as α does in air and with values of α about twice those in pure argon for the same intervals of t' and t.

5. This leads to the inevitable conclusion that *the free electrons do not increase α by recombining at higher rate with positive ions* than do negative ions. In fact the free electrons may even retard recombination. The net result which would determine this effect is hard to estimate as the greater diffusion of the electron gives the values at short t and t' in argon corresponding to long t and t' in air. A lowering of α by free electrons can only occur if electrons recombine with positive ions at a rate which is slower than the normal rate of recombinations of positive and negative ions in argon.

6. This conclusion, that electrons do not participate materially in determining α, is in agreement with the results of Kenty [7] on the recombination of electrons with positive ions in very much purer argon than is used in the usual recombination measurements. By an indirect method, Kenty estimated α in argon to be 10^{-10} instead of 10^{-6} as observed for positive and negative ions. Thus the α, observed in pure argon by Marshall was neither characteristic of α, for ions in argon, nor for electrons. It was probably a function of the rate of attachment of electrons to molecules of impurity ever present in argon, as used in measurements of this sort, to form negative ions, which in turn recombined with the positive ions at the usual rate. The value of α observed in relatively pure argon should, then, vary with the degree of purity, which in devices of the nature used, having metal walls, is never a very high purity.

It is the bearing of certain of these results on the theory of recombination that it is the purpose of this paper to discuss.

1. THE FUNDAMENTAL MECHANISM OF RECOMBINATION.

When it was observed experimentally that the value of α was high for short time intervals, rapidly becoming less and approaching a probably constant value, it was obvious that the fundamental trend of the motion of the ions, with respect to each other, must be towards random distribution, rather than the reverse, as postulated by the theory of Langevin. Langevin has assumed that, since one ion (say a negative ion) is attracted by an ion of opposite sign (a positive ion) according to the Coulomb law of force, e^2/r^2, where e is the charge on the ions and r the distance between them, one could regard the action as follows. Assume one ion (say the positive) fixed. Then the rate of approach of the negative ion, toward the positive ion, leading to recombination, may be expressed by the sum of the mobilities of the two (their relative velocity of drift in unit field) multiplied by the field, due to the positive ion, at the place where the negative ion happened to be. Now for two bodies in space, acting on each other according to the Coulomb law of force, independently of other bodies, this treatment is justified. Again, were both bodies in a space, which exerted a viscous drag, $f = 6\pi\eta av$, as given by Stokes' law, it is probable that one could proceed in the same manner. In the case of two ions, in a real gas, the matter is quite different. While the drift of the ions (mobility) can be described by an equation of the form $f = bv$, where b is a constant, the mechanism by which b is created cannot be considered as due to a viscous liquid, such as Stokes' law demands. The ions are not as if isolated in space in a viscous medium but *they are each subjected, independently of each other, to forces of molecular impact in completely random directions, of magnitudes such that the average energy of impact is many times the potential energy of one ion in the field of the other, except at relatively close approach.* Thus one cannot set one ion as fixed with the other moving towards it, for both ions are being moved by completely random forces, external to themselves, of considerable magnitude. It is thus obvious that the Langevin theory, as originally deduced, is untenable. The problem remains, however, to determine the extent of the action of the forces on the ions in order to see whether one is justified in adopting

the Thomson[2] point of view. It seemed natural to study the relative motion of the ions, by superposing the action of their electrical fields, on each other, on the original Brownian movement equations.[8] Through the kind assistance and inspiration of Professor Arnold Sommerfeld, the writers were able to arrive at a simple approximate solution of the problem, for the general three dimensional case, which suffices for the purposes of discussion.

Let u_1 = vector velocity of particle 1 = $\dot{w}_1$,
u_2 = vector velocity of particle 2 = $\dot{w}_2$,
w_1 = position vector particle 1,
w_2 = position vector particle 2,
B = the coefficient of viscous drag in the medium,
X_1 = unbalanced force on particle 1,
X_2 = unbalanced force on particle 2,
e = charge on ion,
r = scalar distance between ions.

$$(1) \qquad m\dot{u}_1 = -Bu_1 + X_1 + \frac{e^2}{r^2}\left(\frac{w_2 - w_1}{r}\right),$$

$$(2) \qquad m\dot{u}_2 = -Bu_2 + X_2 + \frac{e^2}{r^2}\left(\frac{w_1 - w_2}{r}\right).$$

Multiply (1) by w_1 and (2) by w_2.
Then since

$$w_1 u_1 = \frac{1}{2}\frac{d}{dt}(w_1^2),$$

$$w_1\dot{u}_1 = \frac{d}{dt}(w_1 u_1) - u_1^2,$$

it follows that

$$m\left[\frac{d}{dt}(w_1u_1 + w_2u_2) - (u_1^2 + u_2^2)\right]$$

$$= -\frac{B}{2}\frac{d}{dt}(w_1^2 + w_2^2) + X_1w_1 + X_2w_2$$

$$+\frac{e^2}{r^3}[(w_2 - w_1)w_1 + (w_1 - w_2)w_2].$$

Now

$$[(w_2 - w_1)w_1 + (w_1 - w_2)w_2]$$
$$= [(w_2 - w_1), (w_1 - w_2)] = -r^2.$$

Taking the displacements for times which are sufficiently large as we shall do, the positive and negative values of X_1w_1 and X_2w_2, must cancel out, and we can drop these two terms. Also $m(u_1^2 + u_2^2)$ is, on the average, $4(\frac{3}{2}kT)$ where k is the Boltzmann constant and T is the absolute temperature. Hence

$$(3) \quad m\frac{d}{dt}(w_1u_1 + w_2u_2) = -B\frac{d}{dt}(w_1^2 + w_2^2) + 6kT - \frac{e^2}{r}.$$

We now wish the time average of the integral of this equation over periods of time τ such that r does not vary by too large an amount; i.e. we wish to know the velocity of diffusion for a given value of r. This is found as follows

$$(4) \quad \frac{m}{\tau}\int d(w_1u_1 + w_2u_2) = -\frac{B}{2\tau}\int d(w_1^2 + w_2^2) + \frac{6k\tau}{\tau}\int_0^\tau dt - \frac{1}{\tau}\int_0^\tau \frac{e^2}{r}dt.$$

The integral $\int d(w_1u_1 + w_2u_2)$ vanishes for finite values of τ of the orders to be used in discussion. Also let

$$\Delta_1 = w_1^2 - w_0^2 \quad \text{and} \quad \Delta_2 = w_2^2 - w_0^2.$$

Then

$$\Delta_1 + \Delta_2 = w_1^2 + w_2^2 - 2w_0^2, \text{ and } d(\Delta_1 + \Delta_2) = d(w_1^2 + w_2^2).$$

It is also required to know r as a $f(t)$. Since, in general, this is a diffusion phenomenon, r may be expressed to a first approximation by the expression $r = r_0 + a\sqrt{t}$, where a is a constant. Performing the integration, indicated, and expressing the resultant logarithmic solution in terms of the first two members of its expansion in series, we find, to a rough approximation, that

$$\frac{1}{\tau}\int_0^\tau \frac{dt}{r_0 + a\sqrt{t}} = +\frac{r_0}{\tau},$$

whence we have

$$(5) \quad \Delta_1 + \Delta_2 = \frac{2}{B}\left(6kT - \frac{e^2}{r_0}\right)\tau = 2\frac{6kT\tau}{B}\left(1 - \frac{e^2}{6r_0kT}\right).$$

B for an ion may be found from $u = KX$ and $f = Xe = Bu$, where X is the field strength, K the ionic mobility, and e the ionic charge. Whence $B = e/K$ so that

$$\Delta_1 + \Delta_2 = \frac{2K}{e}(6kT\tau)\left(1 - \frac{e^2}{6r_0kT}\right).$$

Multiplying numerator and denominator by N_A, the Avogadro number, and remembering that

$$\frac{6KN_AkT}{N_Ae} = \frac{6KRT}{N_Ae} = \frac{6KP}{N_A{}^1e} = 6D,$$

when P is the pressure, $N^1{}_Ae$ is the Faraday per molar volume, and D is the coefficient of diffusion for gaseous ions,[9, 10] we have

$$(6) \quad \Delta_1 + \Delta_2 = 2\left\{6D\tau\left(1 - \frac{e^2}{6r_0kT}\right)\right\}.$$

For a single ion diffusing $\Delta_1 + \Delta_2 = 2\Delta$ and we see that

$$(7) \quad \Delta = 6D\tau\left(1 - \frac{e^2}{6r_0kT}\right).$$

It is, of course, understood that Δ is the averaged square displacement in space. If one disregards the factor in parentheses in equation (7), one sees that the equation is the well known equation for the diffusion of a particle in three dimensions.[11] Also, excepting the expression in parentheses, in equation (5), the equation is the well known Brownian movement expression for the separation of two uncharged particles in a given time τ.

The term in parentheses indicates that, for values of $e^2/6r_0kT$ less than unity, the drift of the ions apart, on the average, is less than when the forces are absent, but in the same general direction. This effect on the drift is small except for values of r_0 or T where the term $e^2/6r_0kT$ approaches

1. The value of r_0, for which the drift apart becomes very much reduced, is given approximately by $r_0 = e^2/6kT = 1 \times 10^{-6}$ cm. in air, at 0° C. and *NTP* or 0.1 of a mean free path. While this is merely an approximation, it leads at once to the important conclusion that, except when the ions are within 1 to 10 molecular mean free paths of each other, at N.T.P., the effect of the charges on the motion and diffusion is completely negligible, a conclusion in agreement with the results of Marshall and Plimpton. Thus the assumption, by Thomson, that, up to within a free path or two at N.T.P. or within 10^{-5} cm. of each other, it is the random heat motion that constitutes the important mechanism in bringing the ions together, is completely justified. It is further obvious that, even at 1 mean free path, except at pressures much above an atmosphere, the general trend of the ions will be apart. Hence the *lingering* of ions which fail to unite in a single close approach (conditioned by the situation at and below one atmosphere pressure), postulated by Cravath is a minor factor. Above an atmosphere, especially between 5 and 10 atmospheres, the mean free path becomes comparable with the point at which the separation of the ions becomes very slow. It is not surprising, then, to find that, at such pressures, almost every encounter between opposite ions as defined later leads to recombination.

Below r_0 the expression becomes mathematically indeterminate, but physically it is clear that for smaller distances than r_0 the ions will on the average drift together.

It is of interest to compare the values of the time intervals, characterizing the attainment of more or less random ionic distribution, in Marshall's experiment, with the values of the time expected from the diffusion of the ions, neglecting the effect of the forces as we are now justified in doing. The ions can diffuse from a point to a distance

$$\overline{\Delta x} = \sqrt{\frac{2}{\pi}}\Delta$$

in a time τ to be calculated from the relation

$$\Delta = 6D\tau, \quad \Delta x = \sqrt{\frac{\pi}{2}6D\tau}.$$

Now it can be estimated that a random distribution of 10^{+6} ions per cm.^{3} requires that a drift of from 10^{-3} to 10^{-4} cm. apart to 10^{-2} cm. shall have been achieved, or actually that the ions separate a distance $\overline{\Delta x}$ of nearly 10^{-2} cm. Hence

$$10^{-2} = \sqrt{\frac{\pi}{2} 6 D\tau},$$

and as D for negative ions in air is about .047, we have,

$$\tau = \frac{2}{\pi} \frac{10^{-4}}{6 \times .047} = 2.25 \times 10^{-3} \text{ seconds.}$$

Actually the sharp drop in α observed by Marshall lay within 1.25×10^{-2} seconds. This discrepancy of five fold merits explanation. It is doubtless in part due to the retarding factor of the charges which it is impossible from the approximate relation given to calculate for very long periods of time in which r_0 changes by marked amounts. On the other hand the discrepancy is probably too large to be entirely ascribed to this cause. It is quite possible that it is due to the arbitrary choice of the value of $\overline{\Delta x}$, required, for an *assumed* random distribution, which was set at 10^{-2} cm. The cause for an inaccuracy in choice of $\overline{\Delta x}$ lies in the fact that the ions are not only all more or less situated in pairs, but the pairs are not randomly situated to begin with so that we have a columnar type of ionization, which probably requires larger values of τ to completely erase.

The conclusion to be drawn from the theoretical verification of Marshall's results as regards the importance of diffusion in opposition to Langevin's view, together with the fact that electrons play no direct rôle in the ionic recombination in all gases where they can attach relatively rapidly to form negative ions, allows one at once to proceed to consider the proper theory of ionic recombination in so far as it is possible. This theory was initially proposed by J. J. Thomson [2] in 1924. Unfortunately his original treatment contains a slight error, which the writer reproduced in his Kinetic Theory of Gases. This error was pointed out to the writer by Drs. Mithoff and Cravath in a seminar in 1927. The theory was then correctly deduced but not published owing

to the uncertainty of the fundamental assumptions at that time. In the recent new edition of his book, Conduction of Electricity through Gases (18), Thomson deduces his theory in a different manner and arrives at the same result as that obtained by Mithoff. In view of the fact that the theory constitutes a correct approach to the problem of recombination a brief discussion of the theory may not be out of place. The study of the process consists first of all in the determination of the rate at which the ions of opposite sign drift into the sphere of mutual "active attraction." This rate can be determined by the velocity of thermal agitation of the ions, and the number of ions of opposite sign that such ions encounter per unit time. The deduction furthermore consists in taking account of the fraction of the ions of the sort above mentioned, making a critical encounter, which can succeed in recombining. This treatment therefore requires that some criterion of recombination must be adopted.

Assume that on the average, after the last molecular collision, the ion of one sign moves towards the ion of opposite sign. If it left the last impact with the normal velocity of thermal agitation it will augment its energy relative to its potential partner through the changes of electrical potential, in the field of the other ion, which it experiences. If, then, at closest approach in its orbit, the ion, which is taken as approaching, has an energy of motion (its kinetic heat energy + the gain in energy from the field) greater than the potential energy at closest approach, it will describe an hyperbolic orbit about the opposite ion and go off whence it came to another impact. Such an escape, depending, as the diffusion equation showed, on the relation between the free path L and

$$r_0 = \frac{e^2}{6kT},$$

will determine whether the ions are more likely to continue to separate or drift together again. For the usual conditions in gases at N.T.P. the likelihood of coming together again is distinctly less than that of separation for r_0 is about 1/5, or less, of L (the free path). Thus for ordinary conditions ions having a relative kinetic energy greater than the potential energy at closest approach will separate again, unless by

chance an impact occurs with a neutral molecule so close to the other ion that the energy lost in the impact reduces the energy at the closest distance of approach. Assuming that the impact of one of the ions with a neutral molecule will reduce the energy of the ion to that of thermal agitation, a simple criterion of recombination can be made, which is the approach used by Thomson. This assumption, which is inexact, at least gives a working basis which can later be changed. It might be more correct to assume that both ions must undergo such impacts in order to lose their excess energy, as will later be done here. The problem may be formulated by assuming that if, within a distance defined by d, from the equation

$$\frac{e^2}{d} = \frac{3}{2}kT,$$

the one or the other ion suffers an impact with a neutral molecule which suffices to remove the energy gained in the field since its last impact, the relative kinetic energies of the ions are reduced below the potential energy of the ions and the ions describe closed orbits about a common center of gravity. Such ions were considered by Thomson [2] as having recombined. Actually this assumption is not strictly correct as a subsequent impact with another molecule might restore the energy of the ions lost and so separate them again. However in general and on the average the action of such impacts will be to remove the excess energy gained from the field so that most ions will gradually approach each other and but few will separate again. Ultimately, of course, recombination will probably require an actual physical impact between ions in which the electron transfer can occur.

Based on these considerations J. J. Thomson [18] deduces an expression for d, the coefficient of recombination of ions which may be expressed in the following form:

$$\alpha = \pi d^2\sqrt{U_1^2 + U_2^2}(w_1 + w_2 - w_1w_2),$$

where

$$w_1 = 1 - \frac{2L_1^2}{4d^2}\left\{1 - e^{-2d/L_1}\left(\frac{2d}{L_1} + 1\right)\right\}$$

and

$$w_2 = 1 - \frac{2L_2^2}{4d^2}\left\{1 - e^{-2d/L_2}\left(\frac{2d}{L_2} + 1\right)\right\}.$$

Here d is defined as the radius of the sphere within which an impact with a neutral moledule must occur, and is given by

$$\frac{e^2}{d} = \frac{3}{2}kT,$$

where e is the charge on the ion, k the Boltzmann constant, and T the absolute temperature. U_1 and U_2 are the average velocities of thermal agitation of the positive and negative ions, and L_1 and L_2 are the mean free paths of the same ions. The expression $\pi d^2\sqrt{U_1^2 + U_2^2}$ represents a term related to the number of encounters of ions in the spheres d about each ion, while the term $(w_1 + w_2 - w_1w_2)$ represents a probability ϵ that in such an encounter recombination will follow through collision of one or the other of the ions with a neutral molecule. In view of the fact that the ion is probably more massive than the molecule, one encounter will in general not suffice to reduce the excess energy. Hence it is more likely that recombination will occur, with heavy ions not when just one of the two opposite ions suffers an impact with a molecule, within d, but rather when both ions lose energy in such impacts. We can, therefore, probably more properly determine α not by the chance that the impact described occurs for *one* ion but that *it occurs simultaneously for both ions*.[1] Since the portion of α related to the number of possible recombinations occuring for an encounter at a distance d is given by $\pi d^2\sqrt{U_1^2 + U_2^2}$ and the chance of an impact is w_1 or w_2 for one ion, for both ions simultaneously it is w_1w_2. Since in general L_1 and L_2 are nearly equal $L_1 = L_2 = L$ and we can set $w_1w_2 = w^2$. Thus more properly we might set α as

$$\alpha = \pi d^2\sqrt{U_1^2 + U_2^2}\left[1 - \frac{L^2}{2d^2}\left\{1 - e^{-2d/L}\left(\frac{2d}{L} + 1\right)\right\}\right]^2.$$

The quantities $w_1 + w_2 - w_1w_2$ neglecting w_1w_2, and w^2 can be represented by curves as a function of

[1] One could also do as Richardson [12] tried to do and assume that n impacts inside d were required by each ion, where n must be found. In view of a slight blunder in Richardson's equations and the general uncertainty in experimental results the simple expedient above will suffice for an adequate discussion.

$$\frac{2d}{L} = x,$$

and as

$$d = \frac{e^2}{3/2\,kT} = 4.05 \times 10^{-6}\frac{273}{T},$$

and as

$$L = 1 \times 10^{-5}\frac{760}{p}\frac{L}{L_A},$$

where L/L_A is the value of L relative to L_A, that for air at N.T.P.

$$x = .81\frac{T}{273}\frac{p}{760}\frac{L_A}{L}$$

for a gas at constant density with p in mm Hg, and T in degrees absolute. The values of $w_1 + w_2 = f(x)$ and $w^2 = f(x)^2$ are shown in curves 1 and 2 of Figure 1 for a range of x covering experimental measurements. Again $\sqrt{U_1^2 + U_2^2}$ is the relative velocity of the two ions, and as in absence of any precise knowledge it is simpler to write $U_1 = U_2$, we have

$$U_1 + U_2 = \sqrt{2}\sqrt{\frac{2}{M}}1.84 \times 10^5\sqrt{\frac{T}{273}},$$

where M is the molecular weight and 1.84×10^5 is the velocity of agitation for the H_2 molecule at 273° absolute. Whence α from the two equations proposed becomes available for comparison with experiment as

$$8.\quad \alpha = 3.8 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2} f\left\{0.81\left(\frac{273}{T}\right)\left(\frac{p}{760}\right)\left(\frac{L_A}{L}\right)\right\},$$

$$9.\quad \alpha = 1.9 \times 10^{-5}\left(\frac{273}{T}\right)^{3/2}\left(\frac{1}{M}\right)^{1/2} f\left\{0.81\left(\frac{273}{T}\right)\left(\frac{p}{760}\right)\left(\frac{L_A}{L}\right)\right\}^2.$$

If we choose $L_A = L$, $M = 28.8$, and $T = 273$, the values of α obtained are from

$$(8)\qquad \alpha = 2.82 \times 10^{-6},$$

$$(9)\qquad \alpha = 5.64 \times 10^{-7}.$$

Had we, as is more nearly correct, chosen

$$L = \frac{L_A}{5}$$

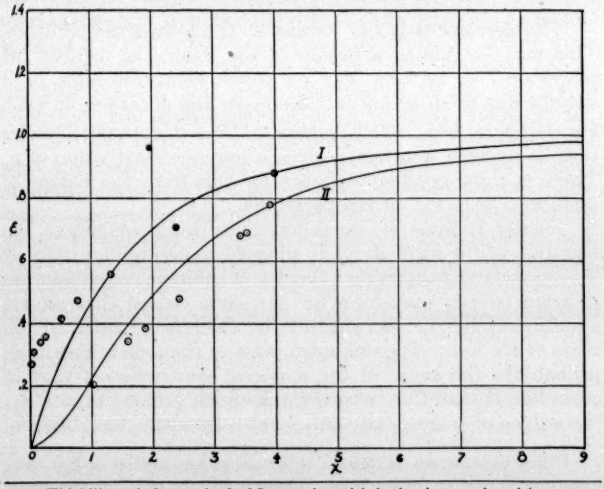
(for the mean free path of ions is about 1/5 the kinetic theory value of that for molecules in air) and had we placed $M = 3$ (28.8) which is possibly more nearly the real mass of the ion the values would become

(8) $$\alpha = 8.41 \times 10^{-6},$$

(9) $$\alpha = 1.62 \times 10^{-6}.$$

It is seen that the values from equation (9) lie more nearly in the region observed by Marshall than do the values from equation (8), but the more proper value is twice Marshall's observed value. As regards the variation of α with pressure, the results of Thirkill,[13] [2] the circled points in Fig. 1, agree

FIG. 1.



[2] Thirkill used the method of Langevin, with ionization produced by x-rays, thus obtaining results which should be fairly reliable. Observations of other workers do not cover as wide a scope as those discussed here, and are, consequently, not given consideration.

more closely with (9) and are incompatible with equation (8) while the results of Hendren [14] [3] differing radically from those of Thirkill agree more nearly with those of equation (8) but deviate from both as shown by the circled crosses of Fig. 1. Obviously no test of the theory is possible with such a diversity of results. In the case of the temperature variation Erikson's [15] results at constant density are compared with the theoretically predicted values from equation (8) after adjusting one value at 285° C. to correspond to Erikson's observed value. The agreement is indicated by the table:

Temp. in °.	Observed.	Calculated.
94°	3.18	5.1
205	2.39	2.16
285	1.47	1.47
337	.94	.90
373	.74	.75
428	.59	.53

The agreement is fair except at the lowest temperature. This may be due to a failure of the theory as regards the power of T to be used, the 3/2 power being too high, or it may be due to an actual *increase in the size of the ion*, at such low temperatures, which makes $\sqrt{U_1^2 + U_2^2}$ really smaller than it appears and hence gives a low observed value of α. There is some possible evidence for this from the values of mobilities at liquid air temperatures.

Finally it must be conceded that, while in general an equation of the form above is adapted to giving in a more or less qualitative fashion the salient facts of ionic recombination it again fails of usefulness for the same reason that all ion equations fail;[17] i.e. because of the unknown nature of the mass of the ion. The unknown mass of the ions is also in all probability the cause of the apparent contradiction that in gases like H_2 and CO_2, where U_{H_2} is much greater than U_{CO_2}, the values of α are nearly the same. In some gases like H_2,

[3] These measurements of Hendren were made with an indirect method, using α particles to produce the ionization. Consequently the columnar effects predominated, serving to mask the variation of α, and the results are not held to be as reliable as those of Thirkill.

N_2, CO, and the inert gases the value of α is influenced by the existence of free electrons, which reduce α as seen for example in the results of Hendren, where in CO having free electrons α is $.87 \times 10^{-6}$ while in CO_2 it is 1.66×10^{-6}, as well as in Marshall's results in argon under similar conditions. Beyond this effect of the nature of the carrier, the value of α is lower than it should be in theory, for after all the negative ions probably never can be simple molecules or atoms of CO, H_2, N_2 or the inert gases, even were ions monomolecular, as these gases do not attach electrons under ordinary conditions. Hence U_H, has always a value which is not characteristic of the gas studied. In H_2 and in air it is doubtful if even the positive ion is an H_2^+ or O_2^+ ion; for mobility measurements in mixtures show that the positive ion in H_2 is a complex having a diameter, as far as mobility measurements go, of about the size of a CH_3NH_2 molecule.[16] Thus the molecular weights even of the simplest ions in gases are completely unknown so that the velocities U are not certain. Hence in view of the fact that the important parameter in the evaluation of α is the velocity of thermal agitation U, and in view of the fact that this depends on the unknown mass of the ion which is in most gases determined largely by active impurities we cannot predict α in absolute value at all. Furthermore as the impurities present in most gases studied with the same technique are more or less similar, organic molecules from stopcock greases, etc., this will largely determine α and give a nearly constant value, independent of the nature of the gas. It is also conceivable that this fact will lead to a gradual decrease in α with time as the ions can increase their mass by picking up bulkier, more active, and rarer molecules of impurity.[17] Were our measurements and theory of recombination more certain the value of the ionic mass might be determined from such results.

BIBLIOGRAPHY.

1. LOEB, L. B. Kinetic Theory of Gases, McGraw Hill, N. Y., 1927, p. 478 f.f.
2. THOMSON, J. J. Phil. Mag. *47*, 337, 1924.
3. LANGEVIN, P. Annales de Chimie et de Physique, *28*, 403, 1903.
4. RÜMELIN, G. Annalen Der Physik, *45*, 821, 1914.
5. PLIMPTON, S. J. Phil. Mag. *25*, 65, 1913.
6. MARSHALL, L. C., Physical Review, *33*, —, 1929.

7. KENTY, C. Physical Review, *32*, 624, 1928.
8. LOEB, L. B. Kinetic Theory of Gases, McGraw Hill, N. Y., 1927, p. 348 f.f.
9. THOMSON, J. J. Conduction of Electricity in Gases, 2nd Edition, Cambridge, 1906, p. 43.
10. TOWNSEND, J. S. Electricity in Gases, Oxford, 1914, p. 91.
11. TOWNSEND. Loc. Cit., p. 90.
12. RICHARDSON, O. W. Phil. Mag. *10*, 242, 1905.
13. THIRKILL, H. Proc. Roy. Soc. London, A88, 488, 1913.
14. HENDREN, L. L. Physical Review, *21*, 514, 1905.
15. ERIKSON, H. A. Phil. Mag. *18*, 328, 1909.
16. LOEB AND DYK. Proc. Nat. Acad. Sci. *15*, 146, 1929.
17. LOEB, L. B. Physical Review *32*, 81, 1928.
18. THOMSON, J. J. Conduction of Electricity Through Gases, III edition, Cambridge, 1928, p. 44.

THE EQUATION OF STATE OF A MIXTURE DETERMINED FROM THE EQUATIONS OF STATE OF ITS CONSTITUENTS.

BY

W. EDWARDS DEMING AND LOLA E. SHUPE,

Fertilizer and Fixed Nitrogen Investigations, Bureau of Chemistry and Soils
U. S. Department of Agriculture.

THE determination of the equation of state for a mixture from the equations of state for the pure component gases has received attention since the time of van der Waals. In a recent paper Dr. Kleeman [1] has given a method by which the equation of state of a mixture may be derived from those of its constituents. Let the equation of state

$$P_i = F(m_i/v,\ T,\ a_i,\ b_i,\ c_i,\ \cdots) \tag{1}$$

for m_i grams of the pure gas i of unvarying molecular species, when expressed in powers of $1/v$, be

$$P_i = \sum_n A_{in}\left(\frac{m_i}{v}\right)^n. \tag{2}$$

The A_{in} are functions of temperature and of the particular gas. The most general equation for a mixture of two gases r and s showing no chemical combination, could then be written

$$P = \frac{(A_{r1}m_r + A_{s1}m_s)T}{v} + \frac{A_{r2}m_r^2 + A_{s2}m_s^2 + f_2(T)m_rm_s}{v^2} + \frac{A_{r3}m_r^3 + A_{s3}m_s^3 + f_3(T)m_r^2m_s + f_3^1(T)m_rm_s^2}{v^3} + \cdots. \tag{3}$$

We shall assume that F has the same form for all components. If $f_2(T) = 2\sqrt{A_{r2}A_{s2}}$, $f_3(T) = 3\sqrt[3]{A_{r3}^2A_{s3}}$, $f_3^1(T) = 3\sqrt[3]{A_{r3}A_{s3}^2}$, $\cdots$, (3) becomes

$$P = \sum_n (\sqrt[n]{A_{rn}}m_r + \sqrt[n]{A_{sn}}m_s)^n v^{-n}. \tag{4}$$

[1] R. D. Kleeman, J. FRANKLIN INSTITUTE, *206*, 511 (1928).

This is Kleeman's equation (11) on page 515 of the reference cited.

The equations for a mixture must reduce to (1) and (2) if either m_r or m_s becomes zero. (3) satisfies this condition. So does (4). The arguments that led Kleeman to equation (4) could have led him to equation (3). If Dalton's law holds, $f_2(T) = f_3(T) = f_3^1(T) = \cdots = 0$, but equation (4) does not allow this. The evaluation of the product terms (interaction terms) has been the inspiration for several pieces of work in kinetic theory, e.g. the recent one by Lennard-Jones and Cook.[2] A good history is given by Beattie.[3] In (4) the interaction terms are fixed by the A_{in}, but obviously this can not be permitted.

Kleeman evidently considered all the $A_{in} > 0$. The situation is easily handled, however, when any $A_{in} < 0$. In the figure a case is shown where one coefficient (A_{rn}) is negative and the other (A_{sn}) is positive. The ordinate to a curve $n = 1, 2, 3, \cdots$ at any abscissa is the proper nth coefficient for the binary mixture composed of x weight fraction of gas s and $1 - x$ of gas r. To construct such a curve, write $A_{rn} = \epsilon_{rn}|A_{rn}|$, $A_{sn} = \epsilon_{sn}|A_{sn}|$, where ϵ_{rn} and ϵ_{sn} are $+1$ or -1 as the case may be, lay off the distance $\epsilon_{rn}\sqrt[n]{|A_{rn}|}$ at $x = 0$, and the distance $\epsilon_{sn}\sqrt[n]{|A_{sn}|}$ at $x = 1$, and join by a straight line. Let x, $\epsilon|y|$ be the coördinates of a point on this line. Then x, $\epsilon|y|^n$ will be the coördinates of the corresponding point on the curve. ($\epsilon = +1$ or -1.)

This idea is easily extended to a mixture of any number of components.

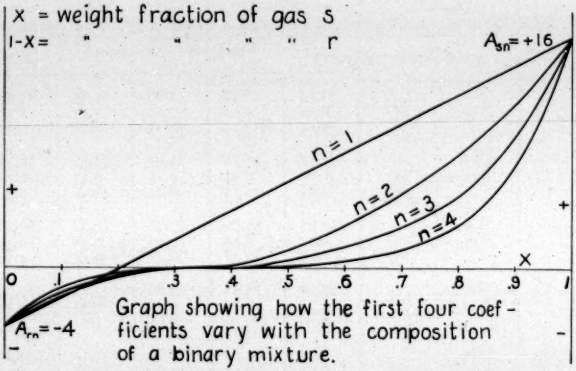
Kleeman's scheme (our equation (4)) can be described as "combination of coefficients." Another scheme is to derive the *parameters* for the equation of state of the mixture from the parameters for the pure components, e.g. by linear combination, as has often been done. Let us refer to it as "combination of parameters." This idea has recently been used by Beattie[3] on mixtures of nitrogen and methane using the Beattie-Bridgeman equation of state. Kinetic theory indicates that "combination of parameters" rests on a firmer

[2] Lennard-Jones and Cook, *Proc. Roy. Soc.*, *115A*, 334 (1927).

[3] James A. Beattie, *J. Am. Chem. Soc.*, *51*, 19 (1929).

theoretical basis than does "combination of coefficients." Lorentz showed that for the first order constants, kinetic theory leads to a quadratic rule for combination of constants, and general considerations indicate that this may be true of any of the constants. Under certain conditions quadratic combination becomes linear combination. Although all equations of state are more or less empirical, yet the various parameters have some physical significance, whereas the

FIG. 1.



Graph showing how the first four coefficients vary with the composition of a binary mixture.

coefficients after the term in $1/v^3$ must be entirely empirical, or complicated functions of simpler terms. Thus "combination of parameters" would appear to be more rational than "combination of coefficients."

The number m of independent coefficients A_{in} in equation (2) will not be greater than the number of parameters a_i, b_i, c_i, $\cdots$. In forming the equation for a mixture by Kleeman's scheme, the coefficients after the mth would be dependent on the first m coefficients. This is doubtless what Kleeman had in mind when he said these coefficients ". . . should initially be looked upon as being entirely independent of each other. If relations exist between them, they would be expressed by separate equations whose existence we need not consider at present." The expansion in powers of $1/v$ of the Beattie-

Bridgeman equation is finite, containing four independent terms. Thus no coefficient depends on any other and it is very easy to apply both of the above methods. The "combi-

TABLE I.

Comparison of the Observed Pressures with those Calculated by (a) Linear Combination of the Parameters a, b, $\sqrt{A_0}$, B_0, c in the Beattie-Bridgeman Equation of State (as already published by Beattie); (b) Combination of the Coefficients.

69.556% nitrogen, 30.444% methane, by weight.

	Temp., °C.	0°	50°	100°	150°	200°
Volume		Pressures, atmospheres				
30	Obs.	31.64	38.17	44.66	51.13	57.59
	$P_{obs.}-P_{calc.}$ (a)	0.04	0.08	0.10	0.11	0.13
	" " (b)	−0.04	−0.10	−0.17	0.25	0.59
25	Obs.	37.76	45.71	53.63	61.51	69.38
	$P_{obs.}-P_{calc.}$ (a)	0.07	0.11	0.15	0.17	0.19
	" " (b)	−0.04	−0.15	−0.25	0.36	0.86
20	Obs.	46.81	57.00	67.15	77.22	87.28
	$P_{obs.}-P_{calc.}$ (a)	0.12	0.18	0.26	0.28	0.32
	" " (b)	−0.06	−0.22	−0.37	0.58	1.36
15	Obs.	61.68	75.81	89.89	103.82	117.74
	$P_{obs.}-P_{calc.}$ (a)	0.24	0.33	0.47	0.52	0.59
	" " (b)	−0.08	−0.39	−0.64	1.04	2.44
12	Obs.	76.35	94.72	113.01	131.11	149.23
	$P_{obs.}-P_{calc.}$ (a)	0.40	0.54	0.76	0.88	1.07
	" " (b)	−0.09	−0.59	−0.98	1.69	3.96
10	Obs.	90.95	113.86	136.64	159.25	181.66
	$P_{obs.}-P_{calc.}$ (a)	0.65	0.84	1.13	1.39	1.53
	" " (b)	−0.07	−0.79	−1.37	2.56	5.69
8	Obs.	112.93	143.25	173.48	203.31	233.07
	$P_{obs.}-P_{calc.}$ (a)	1.19	1.46	2.04	2.44	2.90
	" " (b)	0.06	−1.08	−1.88	4.26	9.39
6	Obs.	150.93	195.53	239.85	283.62	327.44
	$P_{obs.}-P_{calc.}$ (a)	2.88	3.59	4.77	5.83	7.20
	" " (b)	0.87	−0.95	−2.20	9.06	18.72

nation of parameters" has the advantage, usually, of requiring less computation than the other, because most equations of state develop into an infinite power series in $1/v$, and it might be necessary to combine more than just a few coefficients to

attain the desired accuracy. It is interesting to see which gives the better results. The following tables are Beattie's [3] Tables IV, V, VI, into which we have inserted pressures as

TABLE II.

Comparison of the Observed Pressures with those Calculated by (a) Linear Combination of the Parameters a, b, $\sqrt{A_0}$, B_0, c in the Beattie-Bridgeman Equation of State (as already published by Beattie); (b) Combination of the Coefficients.

31.014% nitrogen, 68.986% methane, by weight.

	Temp., °C.	0°	50°	100°	150°	200°
Volume		Pressures, atmospheres				
29.9456	Obs.	37.70	45.99	54.23	62.42	70.59
	$P_{obs.}-P_{calc.}$ (a)	0.00	0.01	0.03	0.02	0.00
	" " (b)	−0.08	−0.17	−0.42	−0.21	0.13
24.9456	Obs.	44.66	54.81	65.04	74.92	84.91
	$P_{obs.}-P_{calc.}$ (a)	−0.01	−0.01	0.14	−0.02	−0.05
	" " (b)	−0.13	−0.28	−0.51	−0.35	0.14
19.9456	Obs.	54.82	67.95	80.92	93.82	106.68
	$P_{obs.}-P_{calc.}$ (a)	−0.01	0.01	−0.01	−0.05	−0.08
	" " (b)	−0.19	−0.40	−1.01	−0.55	0.22
14.9456	Obs.	71.11	89.48	107.71	125.79	143.70
	$P_{obs.}-P_{calc.}$ (a)	0.03	−0.05	−0.05	−0.09	−0.23
	" " (b)	−0.31	−0.79	−1.84	−1.00	0.31
11.9456	Obs.	86.97	110.90	134.73	158.57	182.03
	$P_{obs.}-P_{calc.}$ (a)	0.29	−0.09	−0.23	−0.16	−0.36
	" " (b)	−0.23	−1.25	−3.02	−1.58	0.48
9.9456	Obs.	102.36	132.46	162.65	192.51	222.07
	$P_{obs.}-P_{calc.}$ (a)	0.52	−0.11	−0.14	−0.20	−0.40
	" " (b)	−0.22	−1.79	−4.16	−2.24	0.83
7.9456	Obs.	126.04	165.87	206.42	246.51	286.10
	$P_{obs.}-P_{calc.}$ (a)	1.85	0.19	0.12	0.07	−0.18
	" " (b)	0.66	−2.44	−6.20	−3.13	1.71
6.9456	Obs.	143.52	191.02	239.94	288.11	335.68
	$P_{obs.}-P_{calc.}$ (a)	3.28	0.74	0.81	0.79	0.57
	" " (b)	1.74	−2.69	−7.45	−3.38	3.06

calculated by Kleeman's scheme. The observed pressures were taken by Keyes and Burks at the Massachusetts Institute of Technology.

TABLE III.

Comparison of the Observed Pressures with those Calculated by (a) Linear Combination of the Parameters a, b, $\sqrt{A_0}$, B_0, c in the Beattie-Bridgeman Equation of State (as already published by Beattie); (b) Combination of the Coefficients.

29.69% nitrogen, 70.31% methane, by weight.

Volume	Temp., °C.	0°	50°	100°	150°	200°
		Pressure, atmospheres				
40	Obs.	28.87	34.97	41.04	47.08	53.08
	$P_{obs.}-P_{calc.}$ (a)	0.00	0.03	0.05	0.06	0.04
	" " (b)	−0.04	−0.07	−0.19	−0.06	0.11
35	Obs.	32.75	39.81	46.82	53.80	60.74
	$P_{obs.}-P_{calc.}$ (a)	0.00	0.04	0.06	0.08	0.06
	" " (b)	−0.05	−0.09	−0.25	−0.08	0.16
30	Obs.	37.84	46.22	54.51	62.77	70.99
	$P_{obs.}-P_{calc.}$ (a)	0.01	0.06	0.08	0.10	0.09
	" " (b)	−0.07	−0.11	−0.35	−0.13	0.21
25	Obs.	44.82	55.09	65.26	75.36	85.41
	$P_{obs.}-P_{calc.}$ (a)	0.02	0.08	0.12	0.13	0.11
	" " (b)	−0.10	−0.17	−0.50	−0.19	0.29
20	Obs.	55.00	68.26	81.35	94.37	107.31
	$P_{obs.}-P_{calc.}$ (a)	0.06	0.14	0.18	0.20	0.19
	" " (b)	−0.12	−0.26	−0.80	−0.30	0.46
15	Obs.	71.30	89.91	108.28	126.48	144.61
	$P_{obs.}-P_{calc.}$ (a)	0.16	0.25	0.32	0.33	0.34
	" " (b)	−0.16	−0.47	−1.42	−0.57	0.83
12	Obs.	87.01	111.45	135.61	159.52	183.31
	$P_{obs.}-P_{calc.}$ (a)	0.37	0.42	0.54	0.61	0.67
	" " (b)	−0.13	−0.70	−2.17	−0.79	1.43
10	Obs.	102.36	133.20	163.66	193.78	223.80
	$P_{obs.}-P_{calc.}$ (a)	0.70	0.74	0.92	1.05	1.26
	" " (b)	−0.02	−0.88	−2.99	−0.96	2.36

In general, the tables show that method (*a*) gives the better results. The exceptions consistently occur where both the temperature is low and the pressure high, that is, method (*b*) apparently gives smaller deviations in the lower left hand corners of the tables. These are the points where one usually expects the widest deviations. Method (*b*) has less rational theoretical basis, is usually more laborious to use and reproduces the data on mixtures of methane and nitrogen less

accurately than the combination of parameters in the Beattie-Bridgeman equation of state.

It is interesting to note that Kleeman, even after deriving our equation (4), gives an equation of state for a mixture of two gases based on van der Waals' equation for a pure gas by combining linearly $\sqrt{a}$, b.

"Combination of coefficients" possesses the advantage that it can be used when isotherms for the pure components have been determined at a single temperature only.

Professor James A. Beattie of the Massachusetts Institute of Technology and Dr. Albert R. Merz of the Bureau of Chemistry and Soils have kindly made several suggestions that have been incorporated into this paper.

Irradiated Ergosterol. R. B. BOURDILLON, CATHERINE FISCHMANN, R. G. C. JENKINS, AND T. A. WEBSTER (*Proc. Roy. Soc.*, 1929, *B*, *104*, 561–583) find that ultra-violet radiation produces three substances or groups of substances when it acts upon ergosterol, which is a sterol, a compound allied to both the fats and the terpenes. They studied the absorption spectrum of each of these substances and also determined its antirachitic power. The product first formed has an absorption spectrum similar to that of ergosterol but twice as intense; the maximum absorption occurs at 280 Angstrom units; this product possesses great antirachitic power, and is probably vitamin D, the fat-soluble vitamin which protects from the occurrence of rickets, and has a curative effect in that disease. The purest preparations obtained apparently contained more than 50 per. cent of vitamin D. Further irradiation gives rise to the second product, which has a strong absorption band with its maximum at 240 Angstrom units, but has no antirachitic power. Still further irradiation converts it into the third product, which exhibits no antirachitic power, and shows no marked absorption.

Maurice I. Smith and E. Elvolve (Public Health Reports, 1929, *44*, 1245–1256) have tested the action of irradiated ergosterol on the rabbit. Repeated doses of 2 milligrams or more of irradiated ergosterol, administered by mouth or by intramuscular injection to adult rabbits, may prove fatal in a relatively short period of time. A dose of 1 milligram or less, given 3 or 4 times a week, appeared to be well tolerated. Large doses produced a more or less well marked increase in the calcium content of the blood, while small doses produced variable results. Larger doses also tended to increase definitely the inorganic phosphate content of the blood serum. Toxic doses gave rise to great increases in the calcium content of certain organs, such as the aorta, the kidneys, and the lungs, but produced no change in other organs, like the liver and the skeletal muscle. These results indicate that care must be used in the therapeutic use of irradiated ergosterol to replace cod-liver oil, but do not deprecate its use.

Foods are irradiated with ultra-violet light, in order to impart to them the properties of vitamin D. Adolph G. De Sanctis, Leslie O. Ashton, and Oliver L. Stringfield (Archives of Pediatrics, 1929, *46*, 297–311) have used irradiated powdered whole milk as a food for human infants. They find that the powdered whole milk must be 100 per cent. irradiated, in order to protect the babies from rickets.

J. S. H.

A MECHANICAL METHOD OF MEASURING SOUND PRESSURE.

BY

B. E. EISENHOUR AND F. G. TYZZER,

Riverbank Laboratories,
Geneva, Illinois.

THE investigation of the physical properties of sound often requires some method of measuring the amplitude, pressure, or intensity of the sound waves being propagated.

A Soundmeter, the instrument here described, has many advantages over existing instruments as it is purely mechanical in its operation and construction, giving a direct reading of the sound pressure without the use of vacuum tube amplifiers or other apparatus.

The principle as applied, requires that the pressure, either positive or negative, in sound waves of various frequencies and intensities be measured, and this is accomplished by the use of a special mechanical rectifying valve. The inertia of this valve is very small so that it will open and close in the short period of time necessary to rectify alternating pressures up to 5000 D.V. or more per second. It will function over a range of pressures varying from less than one dyne per square cm. to several thousand dynes per sq. cm. The efficiency of this type of valve can be made about twenty times that of the pinhole rectifiers[1] described by Professor Barus of Brown University. The investigation of these pinhole rectifiers led to the development of the present type of valves.

The Soundmeter can be made in various ways. A single valve instrument is shown in Fig. 1. It consists of a number of diaphragm units, each unit made of two circular discs sealed at their circumference and attached to the adjacent unit at the center by a conducting passage.

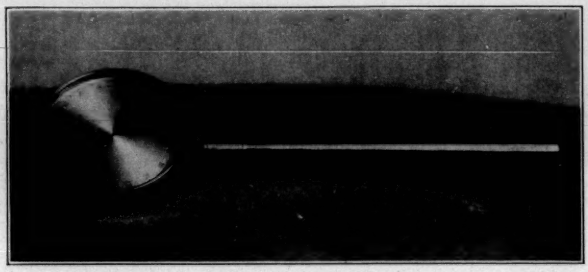
This assembly of units is attached firmly at the center of one side to a support, in such a manner that the opposite side of the assembly can move freely in a vertical direction in

[1] *Pinhole Rectifiers:* Barus, C., *Science*, May, 1921; *Proc. Nat. Acad. of Science*, 8, pp. 163–165 (1922).

response to any change of pressure inside or outside of the diaphragm inclosure.

A double lead screw of 128 threads per inch and .0075 inch in diameter is supported in a vertical position by a fixed nut and a small weight on the lower end of the screw is held by gravity in contact with the top of the diaphragm assembly. A light weight indicator or pointer attached to the top end of the screw is placed over a circular scale at the top of the instrument.

FIG. 1.



Single Valve Soundmeter.

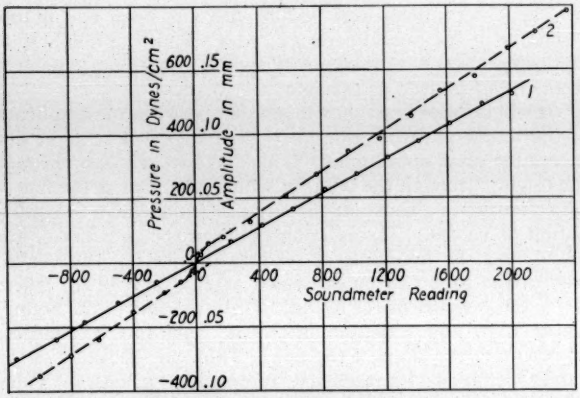
The rectifying valve is placed in the closed end of an adjustable cylindrical resonator $1\frac{1}{4}''$ in diameter and from the valve a conducting passage leads to the diaphragm inclosure. If the resonator is tuned to resonance with the sound being propagated, there will be a maximum change of pressure at the closed end of the resonator and the rectified pressure, either positive or negative, depending upon how the rectifying valve is set, raises or lowers the pressure inside the diaphragm inclosure.

This change of pressure will displace the free end of the diaphragm assembly and by this motion will impart a rotary motion to the screw by moving it through the fixed nut by which it is supported, and the movement of the indicator can be observed on the dial of the instrument.

This dial is divided into 400 scale divisions and, as the maximum reading of this instrument is five revolutions

positive or negative, readings up to 2000 divisions in either direction are possible. The movement of the diaphragm assembly necessary to move the indicator one scale division is .001 mm. and the pressure required is .262 dynes per sq. cm. for the instrument described.

FIG. 2.



Calibration Curves of a Single Valve Soundmeter.
1. Soundmeter readings plotted against static pressures.
2. Soundmeter readings plotted against amplitude of a source of 256 D.V.

In Fig. 2, Curve 1 shows a pressure calibration curve for this single valve instrument in which Soundmeter readings are plotted against static pressures in dynes per square cm. Curve 2 shows Soundmeter readings plotted against amplitude in mm. of the sound source described below.

The static pressures were obtained by measuring the height of the column of water necessary to produce a certain reading of the meter. From the curve giving the sensitivity of the instrument without a valve and from readings of the instrument with a valve, for sounds of known intensity, the efficiency of the valve can be calculated and the instrument calibrated for sound measurement in dynes per square cm. per scale division deflection of the indicator.

In Curve 2 of Fig. 2, the source of sound was a rigid

diaphragm 56 mm. in diameter fastened to a spider mounted upon three wires, the tension of which could be varied for tuning different frequencies. This method of mounting the diaphragm gives essentially the motion of a piston for all displacements. The diaphragm was closely fitted into a baffle plate 170 mm. in diameter and actuated electrically, the double amplitude being measured with a microscope.

The observations were taken with the open end of the resonator of the Soundmeter placed 4″ from the diaphragm, and precautions were taken to change the interference pattern in the room as little as possible.

It will be observed that the relation between the amplitude of the source and the Soundmeter readings is a straight line except for small amplitudes. This line does not pass through the origin, although the point at which it intersects the line of zero pressure is a constant for any particular valve or combination of valves. The relation between the pressure of the sound and the Soundmeter reading (neglecting the curved part of the line) can be expressed as $P = m(S + S_0)$ where (P) is the pressure of the sound, (S) the reading of the Soundmeter (S_0), the constant intercept, and (m) a constant representing the slope of the line. Thus the efficiency of the valves increases with intensity, approaching a constant value when the intercept (S_0) is negligible compared to the meter reading. This intercept (S_0) is a function of the valve construction. In this case it is 90 scale divisions, or 23.6 dynes per sq. cm. The fact that the above equation does not apply to weak sounds does not imply that they cannot be measured, as readings on the curved part of the response curve can be made with considerable accuracy.

Instruments using two valves have been constructed, in which one valve produces a positive pressure inside the diaphragm inclosure and the other produces a negative pressure in the inclosure of the body of the instrument in which the entire assembly is placed. In an instrument constructed in this manner, in which both sides of the wave are used, the reading for a given sound is doubled, allowing the construction of a smaller, more rugged and portable instrument, with a maximum range of twenty or more revolutions. The determination of these large readings is facilitated by a

small indicator which gives the number of complete revolutions of the main indicator. The time necessary to record a given pressure is decreased due to the smaller volume of the inclosures and the reduced inertia of the moving parts.

In the calibration of a sound measuring instrument several methods of determining the intensity of the sound are possible: (1) the measurement of the intensity by means of an electrical or mechanical device; (2) the measurement of the amplitude of the source, either microscopically or from its electrical input and a calculation of the intensity of the sound, and (3), the determination of the intensity in an inclosure by measuring the alternating pressures, or the energy input, or the amplitude of the vibrating portion of its area.

The last of these methods is the most direct and dependable as it gives an absolute measure of the sound, does not depend on a calibration of another sound measuring instrument, is not affected by standing wave systems in the room, and the amplitude to give a certain pressure is independent of frequency if the inclosure is small compared to the wave-length.

A double valve Soundmeter was calibrated in this way by mounting a short tube $1\frac{1}{4}''$ in diameter on the instrument in place of the resonator. A light piston having a bearing surface of about $5/16''$ in length was vibrated electrically in the tube and the amplitude measured with a microscope. In order to reduce friction and prevent leaks the piston was sealed with oil.

The computation of sound pressure in such a small cavity is as follows, for adiabatic compression:

$$PV^{1.4} = K,$$

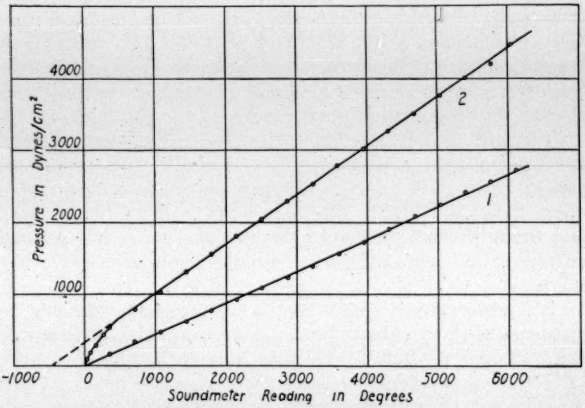
$$dP = -1.4KdV/V^{2.4} = -1.4PdV/V.$$

In this case the area of the piston is equal to the area of the tube so $dV/V = dL/L$ where (dL) is the amplitude of the piston and (L) is the length of the tube. Therefore $dP = -1.4PdL/L$. This equation holds only when the amplitudes are small, and the wave-lengths large compared to the length of the tube. The largest amplitude used in these tests was .06 per cent. of the length of the tube, the resonant

frequency of which was 13,600 D.V., so that the error was negligible.

Fig. 3 shows, in Curve 1, a static pressure calibration, and in Curve 2, a sound pressure calibration for 256 D.V. of a double valve Soundmeter. The sound pressures in Curve 2 were computed from the amplitudes of the piston necessary

FIG. 3.



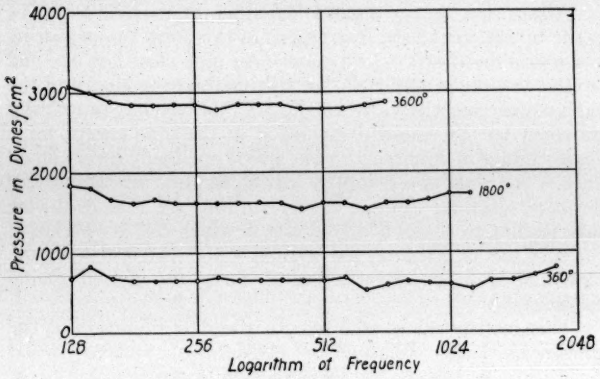
Calibration Curves of a Double Valve Soundmeter.
1. Soundmeter readings plotted against static pressures.
2. Soundmeter readings plotted against calculated sound pressures for 256 D.V.

to give the meter readings. Therefore if the meter recorded the maximum pressure of the sound, Curves 1 and 2 would coincide.

The efficiency of the valves for a given reading of the instrument is the ratio of the ordinates of Curve 1 to Curve 2. As explained above this efficiency approaches a maximum value as the intensity of the sound increases. This maximum value is the ratio of the slopes of the static pressure line and the calculated sound pressure line. For this particular pair of valves it is 64.4 per cent. and the zero intercept is 490 degrees or 216 dynes per sq. cm. Valves have been constructed with a higher efficiency and a zero intercept but these have a restricted frequency range. From these calibrations the

absolute pressure of a sound may be determined. When a resonator is used other factors must be considered but they can be calculated.

FIG. 4.



Pitch Characteristic of a Double Valve Soundmeter.
Pressures to give constant Soundmeter readings at different frequencies.

The curves in Fig. 4, made with constant Soundmeter readings of one, five, and ten revolutions, show that the sensitivity of this pair of valves between 128 and 2048 D.V. is not a function of frequency. The pressures were computed from the amplitudes of the piston necessary to give the constant Soundmeter reading for each frequency as described above. Most of the departures from a straight line are within the limits of observational error, since, in order to avoid resonance at high frequencies, the volume of the cavity was made small necessitating the use of very small amplitudes which were difficult to measure accurately.

An interesting use of the Soundmeter in the exploration of sound patterns is made possible by mounting a valve at the end of a small tube which is connected to the meter. A valve can be constructed with a diameter of about an eighth of an inch so that it introduces very little disturbance in the region to be explored. For example, the pressure along a cylindrical resonator was measured giving results which agreed very well

with theory. In a measurement of the pressure in a $1\frac{1}{4}''$ cylindrical telescoping resonator with several $1/32''$ shoulders, the resulting curve gave an indication of the position of the shoulders.

Absorption measurements [2] of different materials can be made by the use of the instrument in this form by measuring the sound distribution in a cylindrical pipe closed at one end by the absorbing material. In this method the length of the tube connecting the valve to the Soundmeter has practically no effect on the sound distribution in the pipe except for a slight change in volume, for the valve is open only a very small part of the time of a complete vibration after an equilibrium has been reached. This is not true in the case of an exploring tube leading to a telephone receiver in which the free period of the tube has an effect on the original sound distribution in the pipe and on the transmission of energy to the receiving apparatus.

This instrument is adapted: to the determination of the efficiencies either relative or absolute of various sound generating devices, to the investigation of the distribution of sound in standing wave systems, to the determination of pressures or variations in pressures in organ pipes and other wind instruments inaccessible by other methods, to the actuation of relays by a sound of a given pitch and intensity, and to other problems encountered in acoustical research.

[2] *Absorption Measurements:* Weisbach, F., *Ann. d. Physik*, 33, pp. 763–798 (1910). Taylor, H. O., *Phys. Rev.*, 2, pp. 270–287 (1913). Eckhart, E. A., and Chrisler, V. L., Bureau of Standards Bull. 256 (1926). Paris, E. T., Phys. Soc, Proc., 29, pp. 269–293 (1927). Wente, E. C., and Bedell, E. H., *Bell Tech. Jour.*. VII, pp. 1–10 (1928).

HEAT TRANSFER: A LIQUID FLOWING THROUGH A POROUS PRISM.

BY

T. E. W. SCHUMANN,

Combustion Utilities Corporation,
Linden, N. J.

A METHOD often employed in practice for heating or cooling a fluid is to pass it through a mass of crushed material. Vice versa, a mass of crushed material may be heated or cooled by passing a stream of fluid through it.

It is therefore of some importance to formulate the laws governing the rate of heat transfer in such a case, and if possible, to obtain mathematical expressions for the temperature distribution throughout such a system.

A problem of this type which permits of exact mathematical treatment is the following:

Given a right porous prism (or cylinder) consisting of crushed material at a uniform temperature; a fluid, initially at some higher uniform temperature, is allowed to pass lengthwise through the prism at a uniform rate of flow, the sides of the prism being impervious to the fluid. The problem is, to find the distribution of temperature in the prism and in the fluid for all time, assuming that

(*a*) The lumps constituting the prism are so small or have such high thermal diffusivity that any given lump may be considered as being at a uniform temperature at any instant;

(*b*) Compared to the transfer of heat from fluid to solid, the transfer of heat by conduction in the fluid itself or in the solid itself is small and may be neglected;

(*c*) The rate of heat transfer from fluid to solid at any point is proportional to the average difference in temperature between fluid and solid at that point;

(*d*) Change in volume of fluid and solid due to change in temperature may be neglected; and

(*e*) The thermal constants are independent of the temperature.

Under what conditions and to what extent these assumptions are justified can be determined only by experiment. An inquiry into the experimental applications of the theory will not be made in the present paper, the main purpose being to present the mathematical treatment of the problem. For this purpose the following symbols will be employed:

x = distance traversed by the fluid in the prism
t = time
T_0 = initial temperature of the fluid
T_g = temperature of the fluid
T_s = temperature of the solid
h_g = heat capacity per unit volume of the fluid
h_s = heat capacity per unit volume of the solid
f = fractional porosity of the solid, i.e., free space per unit volume
W = volume of fluid passing unit cross-section in unit time
$v = W/f$ = average linear velocity of the fluid
k = constant of heat transfer.

The initial temperature of the solid is taken as zero.

Let us consider the transfer of heat to an element of the fluid of unit cross-sectional area contained between x and $x + dx$. The heat imparted to this element by the solid in time dt

$$= - \text{constant} \times \text{difference in temperature} \times \text{the width of the element} \times dt$$
$$= - k(T_g - T_s)dxdt.$$

The heat carried in by the flowing fluid

$$= - \frac{\partial T_g}{\partial x} h_g v f dx dt.$$

The sum of these must be = rise in temperature in time dt

$$\times \text{ the heat capacity of the element}$$
$$= \frac{\partial T_g}{\partial t} h_g f dx dt.$$

The resulting equation is

$$\frac{\partial T_g}{\partial t} + v\frac{\partial T_g}{\partial x} = -\frac{k}{h_g f}(T_g - T_s) = -k_2(T_g - T_s). \quad (1)$$

In the same way, by considering an element of the solid, we find

$$\frac{\partial T_s}{\partial t} = k_1(T_g - T_s), \quad (2)$$

where

$$k_1 = k/h_s(1 - f) \quad (3)$$

and

$$k_2 = k/h_g f. \quad (4)$$

The significance of the constants k_1 and k_2 will be subsequently discussed.

(1) and (2) are the two equations which determine the transfer of heat. In addition to these there are certain boundary conditions which have to be satisfied if the problem is to be solved completely.

Consider the temperature at $x = 0$.

Here

$$T_g = T_0 \text{ for all time,} \quad (5)$$
$$T_s = 0 \text{ at } t = 0,$$

and from equation (2) it follows that at $x = 0$

$$T_s = T_0(1 - e^{-k1t}). \quad (6)$$

If we imagine the prism to extend to infinity in the positive x direction then we can find the temperatures at the farthest point reached by the fluid. At

$$x = vt,$$
$$T_s = 0, \quad (7)$$
$$T_g = T_0 e^{-k2t}. \quad (8)$$

This latter equation is found by following the frontmost element of fluid, which is always in contact with a part of the solid still at zero temperature. If we therefore consider the

heat transfer from this element to the solid we arrive at the equation

$$\frac{dT_g}{dt} = -k_2 T_g \text{ at } x = vt.$$

Integrated, this equation leads to equation (8).

By introducing two new independent variables

$$y = k_2 x/v, \tag{9}$$

$$z = k_1(t - x/v), \tag{10}$$

equations (1) and (2) are reduced to the simpler forms,

$$\frac{\partial T_s}{\partial z} = T_g - T_s, \tag{11}$$

$$\frac{\partial T_g}{\partial y} = T_s - T_g. \tag{12}$$

These can be further simplified by introducing the two new dependent variables U and V, where

$$T_s = T_0(U - V)e^{-y-z}, \tag{13}$$

$$T_g = T_0(U + V)e^{-y-z}. \tag{14}$$

Substituting these values in (11) and (12), we find that

$$\frac{\partial U}{\partial z} - \frac{\partial V}{\partial z} = U + V, \tag{15}$$

$$\frac{\partial U}{\partial y} + \frac{\partial V}{\partial y} = U - V, \tag{16}$$

and by further differentiation

$$\frac{\partial^2 V}{\partial y \partial z} = V. \tag{17}$$

The boundary conditions for U and V will obviously be:

(*a*) when $y = 0$

$$U = e^z - \tfrac{1}{2}, \tag{18}$$

$$V = \tfrac{1}{2}; \tag{19}$$

(*b*) when $z = 0$

$$U = \tfrac{1}{2}, \tag{20}$$

$$V = \tfrac{1}{2}. \tag{21}$$

Our first step will be to solve equation (17) subject to the boundary conditions (19) and (21).

Put

$$\varphi^2 = -4yz \tag{22}$$

then equation (17) reduces to

$$\frac{d^2V}{d\varphi^2} + \frac{1}{\varphi}\frac{dV}{d\varphi} + V = 0, \tag{23}$$

which is a form of Bessel's equation, of which a well-known solution is

$$V = AJ_0(\varphi), \tag{24}$$

where A is a constant and $J_0(\varphi)$ is a Bessel Function of the first kind and of order zero.

The boundary conditions (19) and (21) are both satisfied if $A = \frac{1}{2}$; hence the final solution is

$$\begin{aligned} V &= \tfrac{1}{2}J_0(\varphi) \\ &= \tfrac{1}{2}J_0(2i\sqrt{zy}) \\ &= \tfrac{1}{2}M_0(yz)\,(\text{say}), \end{aligned} \tag{25}$$

where we introduce the function M_0 which is defined thus:

$$\begin{aligned} M_0(a) &= J_0(2i\sqrt{a}) \\ &= 1 + a + \frac{a^2}{(2!)^2} + \frac{a^3}{(3!)^2} + \cdots. \end{aligned} \tag{26}$$

Having obtained the value of V, the next step is to find a solution for U which will satisfy equations (15) and (16) subject to the given boundary conditions.

Integrating equation (15) as an ordinary linear differential equation, we find

$$\begin{aligned} U &= e^z \int e^{-z}\left(V + \frac{\partial V}{\partial z}\right)dz + e^z f(y) \\ &= V + 2e^z \int e^{-z} V dz + f(y)e^z, \end{aligned} \tag{27}$$

$f(y)$ being a function of y. But by means of successive partial integration we find that

$$2e^z \int e^{-z} V dz = -2\left(V + \frac{\partial V}{\partial z} + \frac{\partial^2 V}{\partial z^2} + \cdots\right) = -\sum_{n=0}^{\infty} y^n M_n(yz), \tag{28}$$

where the M functions are thus defined:

$$M_0(a) = J_0(2i\sqrt{a}),$$
$$M_n(a) = \frac{d^n M_0(a)}{da^n}. \tag{29}$$

The series obtained above can be shown to be converging so that the expansion is valid. It follows that

$$U = \frac{1}{2} M_0(yz) + f(y)e^z - \sum_0^{\infty} y^n M_n(yz). \tag{30}$$

Now, when

$$z = 0,$$
$$V = \tfrac{1}{2},$$
$$U = \tfrac{1}{2},$$

and

$$\sum_0^{\infty} y^n M_n(yz) = e^y.$$

Therefore

$$\tfrac{1}{2} = \tfrac{1}{2} + f(y) - e^y,$$

i.e.

$$f(y) = e^y$$

and equation (30) becomes

$$U = \frac{1}{2} M_0(yz) + e^{y+z} - \sum_0^{\infty} y^n M_n(yz). \tag{31}$$

This solution satisfies both the boundary conditions, but it must still be demonstrated that it also satisfies equation (16), which states that

$$\frac{\partial U}{\partial y} - U = -\frac{\partial V}{\partial y} - V. \tag{16}$$

From equations (27) and (28) it is evident that the expression for U can be written in the form

$$U = V + e^{y+z} - 2\left(V + \frac{\partial V}{\partial z} + \frac{\partial^2 V}{\partial z^2} + \cdots\right).$$

Hence

$$\frac{\partial U}{\partial y} = \frac{\partial V}{\partial y} + e^{y+z} - 2\left(\frac{\partial V}{\partial y} + \frac{\partial^2 V}{\partial y \partial z} + \frac{\partial^3 V}{\partial y \partial z^2} + \cdots\right)$$

$$= e^{y+z} - \frac{\partial V}{\partial y} - 2\left(V + \frac{\partial V}{\partial z} + \frac{\partial^2 V}{\partial z^2} + \cdots\right), \qquad (32)$$

since $\dfrac{\partial^2 V}{\partial y \partial z} = V$.

Substituting these values for U and $\dfrac{\partial U}{\partial y}$ in (16), it is evident that (16) is satisfied. Equation (31) therefore gives the value of U which satisfies the conditions of the problem completely.

It can be shown that there exists between the last term in equation (31) and the expression $\sum_0^\infty z^n M_n(yz)$ a certain very simple relation.

To demonstrate this, put

$$B = \sum_0^\infty (y^n + z^n) M_n(yz)$$

$$= -2e^y \int e^{-y} V dy - 2e^z \int e^{-z} V dz. \qquad (32)$$

Now,

$$\frac{\partial B}{\partial y} = -2V - 2e^y \int e^{-y} V dy + 2\frac{\partial}{\partial y}\left(V + \frac{\partial V}{\partial z} + \frac{\partial^2 V}{\partial z^2} + \cdots\right)$$

$$= -2V - 2e^y \int e^{-y} V dy + 2\frac{\partial V}{\partial y} - 2e^z \int e^{-z} V dz$$

$$= B - 2V + 2\frac{\partial V}{\partial y}$$

i.e.

$$\frac{\partial (B - 2V)}{\partial y} = B - 2V. \qquad (33)$$

Similarly

$$\frac{\partial(B - 2V)}{\partial z} = B - 2V. \tag{34}$$

Hence

$$B - 2V = e^{y+z}$$

or

$$\sum_0^\infty (y^n + z^n) M_n(yz) = e^{y+z} + M_0(yz), \tag{35}$$

a fact which may be readily verified by expansion of the expressions and proper rearrangement of the terms.

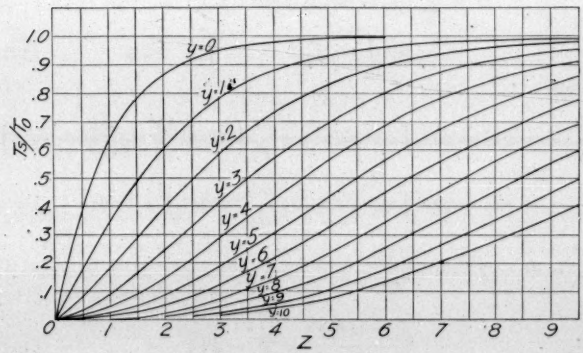
By substituting the values found for U and V in equations (13) and (14), the final solution is obtained

$$T_s/T_0 = 1 - e^{-y-z} \sum_{n=0}^{\infty} y^n M_n(yz) = e^{-y-z} \sum_{n=1}^{\infty} z^n M_n(yz), \tag{36}$$

$$T_g/T_0 = 1 - e^{-y-z} \sum_{n=1}^{\infty} y^n M_n(yz) = e^{-y-z} \sum_{n=0}^{\infty} z^n M_n(yz), \tag{37}$$

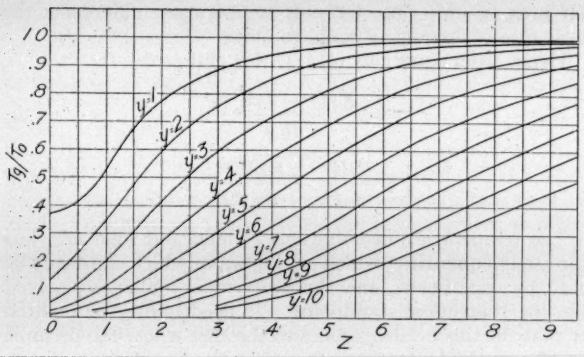
where y, z and the M functions have been previously defined. The numerical values of T_s/T_0 and T_g/T_0 were calculated from equations (36) and (37) for values of y and z ranging from zero to 10, and the results are graphically represented in Figures 1 and 2.

FIG. 1.



Curves showing the temperature in the solid.

FIG. 2.



Curves showing the temperature in the liquid.

From equations (1) and (2) it is evident that k_1 and k_2 both have the physical dimensions of an inverse time, and it follows from equations (9) and (10), which define y and z, that both these quantities are dimensionless. Thus, in the above-mentioned figures, all the quantities involved, namely, T_s/T_0, T_θ/T_0, y and z are dimensionless. The charts are therefore of universal application to all problems of this type no matter what the actual constants involved may be.

There remains the discussion of k as used in the above analysis. For a given value of v, k is equal to the amount of heat transferred in unit time from fluid to solid in unit volume of the prism for unit difference of temperature.

From experiment [1] we know that k is proportional to some power, say the mth power, of the linear velocity and to the area of common surface between fluid and solid. If we denote by s the volume of a particle or lump divided by the area of its surface, then the area of the surface in unit volume of the prism will be $(1 - f)/s$.

Hence

$$k = \frac{K(1-f)v^m}{s} = \frac{K(1-f)W^m}{sf^m}, \qquad (38)$$

[1] See e.g. Gröber, "Wärmeübertragung," p. 87.

where K is defined as the amount of heat transferred across unit area in unit time for unit temperature difference, the linear rate of flow being equal to unity.

Hence from equations (3), (4), (9) and (10)

$$y = \frac{Kx(1-f)W^{m-1}}{sh_g f}, \tag{39}$$

$$z = \frac{KtW^m}{sh_s f^m} - \frac{KxW^{m-1}}{sh_s f^{m-1}}. \tag{40}$$

The temperature distributions in fluid and solid are thus expressed in quantities which are known or which can easily be found by experiment, and the problem is completely solved from the theoretical standpoint. It need hardly be pointed out that the theory also applies to the case where the prism is initially at a higher temperature than the liquid.

As will be readily recognized, the above analysis also applies to the turbulent flow of a liquid through an adiabatically shielded thin-walled pipe.

From the practical point of view, it would be of great value if the same problem could be solved for the transfer of heat from a flowing gas to a prism of crushed material, taking due consideration of the fact that a gas expands with increasing temperature. The mathematical difficulties, however, seem to be insuperable. Nevertheless, there remains a method of at least partially solving this very interesting problem, namely the method of dimensional analysis. The particular method we adopt for this purpose is to write down the differential equations which determine the transfer of heat and from these to draw certain conclusions concerning the dimensional similarity between different systems.

If it be assumed that the gas in question obeys Charles' Law, the differential equations corresponding to equations (1) and (2) can be shown to be

$$\frac{\partial T_s}{\partial t} = \frac{Kv^m}{sh_s}(T_g - T_s), \tag{41}$$

$$\frac{\partial T_g}{\partial t} + v\frac{\partial T_g}{\partial x} = -\frac{K(1-f)v^m T_g}{sh_0 T_0 f}(T_g - T_s), \tag{42}$$

where now

$$v = \frac{WT_g}{fT_0} + T_g \int_0^x \frac{1}{T_g^2} \frac{\partial T_g}{\partial t}\, dx$$

$$= \frac{WT_g}{fT_0}, \qquad (43)$$

since the second term is so small as to be insignificant in all practical cases. The method of derivation of the above expressions is quite straightforward and will not be given here. In equations (41)–(43) all the temperatures should be expressed in degrees absolute, and W = volume of the gas flowing through unit cross section in unit time measured at temperature T_0

h_0 = thermal capacity of unit volume of the gas at temperature T_0.

Examining equations (41) and (42), it will be found that they remain unaltered if

(*a*)	W	is multiplied	by a	factor	M,
	t	"	"	"	M^{-m},
	x	"	"	"	M^{1-m};
(*b*)	s	"	"	"	M,
	t	"	"	"	M,
	x	"	"	"	M.

The conclusions to be drawn from these statements are:

(*a*) If the mass of gas passing through the prism be increased M times the temperature history of a point x will be repeated at a point xM^{1-m} in $1/M^m$ of the original time. In other words if an experiment has been performed on a given system at a given rate of flow, and the temperature distribution has been found throughout the prism for all times, then for any other rate of flow the temperature distribution may be predicted.

(*b*) In the same way, if the linear dimensions s of the solid particles constituting the prism be increased M times the original temperature history at a point x will be reproduced at a point Mx in M times the time. This means that having

experimented with one size of particle, the theory allows us to predict the temperature distribution for a prism consisting of particles of any other size, provided all the other factors remain the same. In the same way some further conclusions may be drawn, but these two examples of dimensional similarity will suffice to illustrate the method.

SUMMARY.

If a liquid, initially at uniform temperature, passes lengthwise through a right, porous prism, initially at some other uniform temperature, the sides of the prism being adiabatic and impervious to the liquid, then the temperatures of both liquid and solid will be functions of the time and of a distance. The problem of finding the temperature distributions has been solved assuming the well-known laws governing the transfer of heat from a liquid in turbulent motion to a solid. The solution as presented involves the use of some interesting mathematical functions which are related to the well-known Bessel Functions. If a gas is used instead of a liquid, the problem is much more complicated, but a dimensional method of treating the problem leads to results which may be very useful in practice.

The author wishes to express his thanks and appreciation to Dr. S. P. Burke for suggesting this research and showing such a stimulating interest during its development, and also to the Combustion Utilities Corporation for permission to publish the results.

MUYBRIDGE'S MOTION PICTURES.

BY

L. F. RONDINELLA,

Member of the Institute.

HAVING served as first assistant for Eadweard Muybridge, in charge of his electrical apparatus and scientific records, during the summers of 1884 and 1885 when he made his photographic investigations of animal motion under the auspices of the University of Pennsylvania, I was much interested in Dr. Henry Leffmann's article in the last June issue of the JOURNAL, and in the earlier article by Mr. George E. Nitzsche on "The Muybridge Moving Picture Experiments" which Dr. Leffmann criticizes. Soon after the publication of Mr. Nitzsche's paper, I prepared an article telling "More About Muybridge's Work," which probably will be published in the next issue of *The General Magazine* of the University; and I should like here to add some explanation and defense of the claim made for Muybridge as the inventor of moving pictures.

Dr. Leffmann's statement that "Muybridge devised and carried out with great ingenuity and success the *analysis* of motion, but the present day screen-play is a *synthesis*," would mislead the reader into thinking that Muybridge did nothing to reproduce on a screen the motions previously analyzed. His first analyses by successive photographic exposures were made of the various gaits of horses in the private stud and on the racing track of Mr. Leland Stanford at Palo Alto, California, and the best of his results were copyrighted in 1878 and published under the title of "The Horse in Motion." During the following year 1879 Muybridge developed an apparatus, which he called the Zoopraxiscope, for making a synthesis from any previously made analysis of motion, by the aid of which he successfully reproduced the moving figures in large size on a screen, and *motion pictures were then born!* In this apparatus the successive phases of the analyzed motion were reproduced around the rim of a large circular

glass plate to be placed on the shaft in his Zoopraxiscope, so that when this instrument was properly attached to an oxy-hydrogen lantern and the shaft and plate were rapidly revolved, the enlarged images were projected successively upon a screen, and the eyes of the audience received the synthesized impression of the original motion, as in modern moving pictures.

Such moving pictures were used by Muybridge to illustrate lectures on animal motion which he gave in 1881 and 1882 in Europe, and in 1883 and 1884 in this country. Because of the then "state of the art" of instantaneous photography, these early pictures showed but little detail, and in a lecture when he exhibited them on a screen before the Royal Institution of Great Britain on March 13, 1882, Muybridge stated: "It is also probable that . . . future and more exhaustive experiments, with the advantages of recent chemical discoveries, will completely unveil all the visible muscular action of men and animals even during their most rapid movements."

For his investigations in 1884 and 1885 Muybridge developed an electro-magnetic latch which released the camera-shutter when current was sent through the magnet, and an automatic contact motor whose essential feature was a circle of twenty-four metallic segments radially insulated and each connected by a wire to one of the shutter-magnets in a battery of twelve or twenty-four permanent or portable cameras, with a return wire from *all* the magnets attached to a radial arm whose outer end carried a metallic brush around the periphery of the circle of segments. The actuating clock-work having been set running at the proper speed, and the motion of the subject being started, the arm was electrically thrown into gear by the operator pressing a push-button at the proper instant, and the successive exposures were made as the subject moved in front of the cameras, with an exact time interval between the phases of motion photographed. He also was then able to obtain photographic dry plates, coated with a special, very sensitive emulsion; and his new batteries of cameras had very efficient lenses.

With these improved methods and apparatus, Muybridge analyzed all kinds of motions of men and women, domestic

and wild animals, and birds. These photographs showed a large amount of detail, and were in every way remarkable achievements for their time. Nearly a thousand sets were made, and 781 of them were beautifully reproduced by photogravure on large sheets and sold in portfolios of 100 plates selected by the purchaser. A large number and variety of them were reproduced from the original negatives as positives on glass disks for the Zoopraxiscope; and when they were used with a projecting lantern, the moving pictures thus shown on a screen were very satisfactory. For several years after the publication of his plates of motion analyses, Muybridge used these syntheses in his Zoopraxiscope to project moving pictures as illustrations in lectures which he gave to describe his work at the University and the published results.

These lectures and moving pictures excited so much interest that "in the summer of 1892 . . . he received an invitation from the Fine Arts Commission of the World's Columbian Exposition to give a series of lectures . . . in association with the Exposition"; and upon his acceptance of this invitation, the Commission "erected for this special purpose on the grounds of the Exposition, a commodious theater," labeled with the jaw-breaking name of "Zoopraxographical Hall," but generally spoken of as "the moving picture theater." Here, during this World's Fair in 1893, Muybridge gave (to pay-audiences) illustrated lectures which, in his "Descriptive Zoopraxography" published that year, he describes as follows: "The course usually adopted is to project, much larger than the size of life upon a screen, a series of the most important phases of some act of animal motion,—the stride of a horse while galloping, for example,—which are analytically described. These successive phases are then combined in the Zoopraxiscope, which is set in motion, and a reproduction of the original movements of life is distinctly visible to the audience. With this apparatus, horse-races are reproduced with such fidelity that the individual characteristics of the motion of every animal can readily be seen; flocks of birds fly across the screen with every movement of their wings clearly perceptible; two gladiators contend for victory with an energy which would cause the arena to resound with wild applause; athletes turn somersaults; and

other actions by men, women, and children, horses, dogs, cats, and wild animals,—are illustrated in the same manner. By this method of *analysis and synthesis* the eye is taught how to observe and to distinguish the difference between a true and a false impression of animal movements."

In the early 90's flexible photographic film had been perfected and used, and the scope of the motions photographed was thereby greatly increased. But motion picture machines equipped with film photographs were not publicly shown until 1895 in Atlanta, and 1896 in New York City. In view of the established facts that Muybridge was the first to project motion pictures upon a screen (in 1879),—that with the improved methods which he devised and used in his University work the scope and quality of his motion pictures were much enhanced (from 1885),—and that he operated the first theater in which motion pictures were commercially shown (in 1893),—I think that there is *ample* "justification for declaring Eadweard Muybridge to be the inventor of motion pictures."

July 12, 1929.

Dr. Howard McClenahan, Secretary,
The Franklin Institute.

Dear Sir: Referring to Professor Rondinella's communication, printed above, I wish merely to say that documentary evidence is in possession of The Franklin Institute showing beyond a doubt that on February 5, 1870, Henry R. Heyl, a member of the Institute, exhibited on a screen at the American Academy of Music in this city, at a public lecture before a large audience, a series of pictures taken from living models and synthesized so as to reproduce the illusion of motion. The synthesis was so exact as to permit the motion of one scene (a waltzing couple) to be synchronized with appropriate music. A claim that Eadweard Muybridge was the "inventor" of motion pictures cannot be sustained in the face of historical data available.

With respect,

HENRY LEFFMANN.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

OPTICAL ROTATION.

THE practical application of the polariscope has greatly increased during the past few years, and this instrument is now indispensable in many of the control laboratories of industrial plants. However, the fundamental principles of the rotation of the plane of polarization, until recently were no better understood than they were when Van't Hoff and Le Bel discovered the coincidence of optical rotation with the presence of an asymmetric carbon atom. The bureau has now observed a relationship between optical rotation and atomic dimension which may bring the phenomenon of optical rotation out of its isolated position and into relationship with other physical constants.

The study of this relationship has already increased our knowledge of carbohydrate chemistry. Many new sugar derivatives have been prepared, and structure formulas of more complicated carbohydrates, such as cellulose, can be derived by the application of this relationship. Since many derivatives of cellulose have important practical applications, as in photographic films, artificial silk, explosives, etc., it is desirable to have a better understanding of its properties. This is a good example of the practical results which are often obtained as by-products of a scientific investigation.

A peculiarity of the observed relationship is that the specific and not the molecular rotation is related to the atomic dimension. Whether or not this peculiarity will hold also for compounds containing only one asymmetric carbon atom is now being investigated. Two isometric, optically active amyl alcohols are required in pure form in such quantities that the halogen derivatives (fluorine, chlorine, bromine, and iodine) may be prepared from them, excluding racemization. This work has necessarily taken many months, but a few liters of the first of these alcohols have already been obtained and a

* Communicated by the Director.

process for deriving the other has been developed. Both will eventually be available in the required quantities.

FUNDAMENTAL RESEARCH ON LUBRICATION.

SEVERAL investigations of theoretical and practical interest recently completed by members of the bureau staff will provide the preliminary groundwork for a new program of unusual importance to be conducted in the bureau's laboratories in coöperation with the leading manufacturers of steam, electrical, automotive, and marine equipment, machine tools, and other products. The new program is sponsored by the American Society of Mechanical Engineers and the work itself will be supervised by the Special Research Committee on Lubrication of that Society. This committee is the oldest one of the many special research committees of the A. S. M. E. It was organized in 1915 to promote fundamental research in lubrication and to coördinate both American and foreign information on that subject. The present personnel of the committee comprises ten members representing executives, engineers, and educators who have been familiar with the problems and applications of lubrication and bearing design and who are well known in the mechanical engineering profession.

Probably very few persons outside the ranks of mechanical engineers have any accurate comprehension of the importance of friction and lubrication problems in relation to every day life. We speak of the elimination of waste, forgetting that energy as well as material is capable of conservation. This can perhaps be attributed to the fact that power and energy are intangible and invisible; in any event it is a fact that very nearly the entire amount of all mechanical power generated for industrial or social use, illumination excepted, is destroyed by friction and dissipated into heat. In fact, the power is not only lost, but the heat produced locally in the bearings may be a harmful agent in itself.

Friction losses can be reduced by scientific selection and development of lubricants which need not be limited to petroleum oils; by a determination of the most efficient operating conditions for existing equipment, as regards ap-

plication of the lubricant, and control of speed, load, and temperature factors; and finally by a more rational design of new machinery, utilizing all the aid that can be obtained from a theoretical and empirical study of the mechanics and thermodynamics of lubrication.

The preliminary experimental groundwork referred to above has included: (1) The effect of "running-in" on the performance of journal bearings. (2) The effect on journal bearing performance of changes in the length of the bearing and the clearance or closeness of the fit. (3) Development of simple types of apparatus for observing (*a*) pressure distribution at all points around the circumference of a journal bearing, and (*b*) occurrence of metallic contact as affected by load, speed, and position of oil inlet. (4) Determination of the increase in viscosity of lubricating oils due to high pressures and also the change in the temperature-coefficient of viscosity due to high pressures. (5) Study of the cause of clogging of capillaries when flow continues for some period of time. (6) Construction of four types of machines for quantitative measurement of the elusive characteristic called "oiliness."

These six investigations may be very briefly summarized as follows:

(1) *Effect of Running In.*—The friction loss of a well run-in bearing may be as little as half that of the same bearing when new. At the same time the well-known minimum point, which marks the transition from unstable to stable lubrication, is progressively shifted toward lower speeds and heavier loads, thus increasing the factor of safety with respect to overloading and overheating. This research showed quantitatively for the first time what actually happens when a bearing is "run-in" or allowed to "wear in" due to continued use. A full discussion of the original paper by S. A. McKee will be found in the July, 1928, issue of *Mechanical Engineering*, Volume 50, pages 528–533 (not previously cited in *Technical News Bulletin*).

(2) *Effect of Length and Clearance.*—The accepted theoretical formula for the effect of clearance was verified under moderate loads and high speeds, namely, that the friction varies inversely as the clearance. There exists, however, no

theoretical formula for the effect of varying the length of the bearing, except when the film is of uniform thickness and the bearing is long enough to neglect the escape of oil and loss of fluid pressure at the ends, in which event the coefficient of friction is directly proportional to the length of the bearing. In these experiments 21 different sets of bearings were tested ranging from a clearance-diameter ratio of 7.5 parts in ten thousand up to one per cent. of the diameter, and from a length-diameter ratio of 2.8 down to as short a bearing as one-quarter of the diameter. The friction for short bearings was found to be considerably greater than would be computed from formulas neglecting the end effect and has been expressed in the form of an empirical curve plotted against the length-diameter ratio as abscissa. The ordinate of the curve represents the correction to be added to the coefficient of friction as computed from the long-bearing formula. Practically the same curve applies to all clearances within the limits covered by these experiments. The correction value is approximately 0.013 for a length diameter ratio of one quarter, and drops to about 0.002 for length diameter ratios equal to or greater than three quarters. The original paper by S. A. and T. R. McKee should be consulted for further details. An extended abstract appears in the August, 1929, issue of *Mechanical Engineering* Volume 51, pages 593–595.

(3) *Pressure Distribution and Metallic Contact.*—The journal or shaft running in a heavily loaded bearing is eccentrically located which permits the formation of a wedge shaped oil film. Fluid pressures are generated in the converging portion of the film which come to a maximum at some point on the circumference and thus the loaded journal is supported on a liquid film under normal operating conditions. To calculate the load carrying capacity of a bearing it is necessary to know the form of the curve for pressure distribution around the circumference. In short bearings or bearings of any moderate length this must be determined by experiment. A comparatively simple device which can be mounted in a vertical drill press had been devised for this purpose by S. A. McKee several years ago and the results already obtained show in what direction the actual pressure distribution differs from that calculated for long bearings.

The device for demonstrating metallic contact operates with a horizontal journal bearing, having a small incandescent lamp in the circuit which flashes on when the film thickness at point of nearest approach has been sufficiently reduced. The design of this apparatus with its arrangements for regulating the several operating variables is due to S. A. McKee. It has served a useful purpose in demonstrating the laws of lubrication and is capable of further development with the object of quantitative measurements. Two models are on exhibit in different divisions of the Bureau of Standards; a third has been requested by the Museum of Peaceful Arts in New York City.

(4) *Viscosity under Pressure.*—The most familiar property of a lubricating oil is its viscosity or resistance to flow and it is one of the vital factors in determining both friction loss and load carrying capacity of bearings. The viscosity must be neither too high nor too low if satisfactory operation is to be secured. It is well known that the viscosity of any oil falls off rapidly with rise of temperature, the fact however that viscosity increases with pressure is a more recent discovery. The effect of high pressure is not only to increase the absolute viscosity, but also to increase the temperature coefficient or rate of change of viscosity with respect to temperature. Recent investigations in England and Germany have corroborated and extended the results first published in 1916 by M. D. Hersey of the bureau staff. Further data and general discussion of the possible significance of these results will be found in papers by S. Kiesskalt, Forschungsarbeiten No. 291, published by the Verein deutscher Ingenieure, 1927; by M. D. Hersey and Henry Shore, "Viscosity of Lubricants under Pressure," *Mechanical Engineering*, Volume 50, 1928, pages 221–232, and by M. D. Hersey, "Fundamental Action of Lubricants," *American Machinist*, June 13 and 20, 1929.

(5) *Clogging of Capillaries.*—This recent work by R. Bulkley, conducted in part at Johns Hopkins University, is a preliminary to the study of oil flow through extremely fine metal capillaries. The ultimate object is to determine how thin a film must become before the influence of the metal molecules makes itself felt to such an extent that the properties of the liquid are no longer the same as in bulk. It has been

found that the progressive clogging effects which had been attributed in the literature to adsorption on the walls of the capillary are due to minute particles of foreign matter which can be removed by special methods of filtering.

(6) *Measurement of Oiliness.*—Preliminary results have been obtained on four different types of oiliness machines which have been described in the article on "Fundamental Action of Lubricants" cited above. They provide the necessary starting point for reducing the quality of oiliness to a quantitative, standardized measurement which will form an important part of the new program for research in coöperation with the American Society of Mechanical Engineers.

INVESTIGATION OF DAMPING LIQUIDS FOR AIRCRAFT INSTRUMENTS.

IN coöperation with the National Advisory Committee for Aeronautics the Bureau of Standards has been obtaining experimental data on liquids suitable for use in aircraft instruments. At present damping liquids are used in aircraft compasses and lateral inclinometers. Artificial horizons of the bubble type depend for their operation on liquids having the same characteristics which are important in a damping liquid.

After giving due consideration to the factors of invariability with time, low volatility, constancy of index of refration and transparency for varying temperatures in the choice of the liquids, data were obtained on the freezing point and on the viscosity in the temperature range $-20°$ C. to $+30°$ C. The latter property is of primary importance in the selection of a damping liquid.

The freezing point of the liquids should be $-40°$ C. or lower since aircraft instruments may be subjected to low temperatures during the ordinary operation of aircraft.

Measurements of the viscosity were made on solutions of animal, vegetable and mineral oils in xylene, glycerine in alcohol, and other solutions. Data were obtained for individual liquids including kerosene, mineral spirits, xylene and recoil (mineral) oil. These data are published in N. A. C. A. Tech. Report No. 299 which may be obtained for 10 cents from the Superintendent of Documents.

The object of the investigation was to find a liquid or liquids which had a high viscosity at about 25° C., and small temperature coefficient of viscosity. A criterion for comparing the liquids in this respect is arbitrarily selected as the temperature at which the kinematic viscosity is five times that at +30° C. For most purposes this fixes the lower temperature limit of usefulness. No liquids with an absolute viscosity greater than 0.05 poise at 25° C. were found for which this temperature is much below −20° C. and none of absolute viscosity of about 0.025 poise with this temperature below −40° C.

Further work is being carried on, first, in extending the lower temperature limit of the data to −50°, C. and lower and second, in obtaining data on promising liquids and solutions in an effort to find those with a viscosity higher than 0.025 poise at 25° C. which are usable at temperatures down to −40° C.

A COURSE-SHIFT INDICATOR FOR THE DOUBLE-MODULATION TYPE RADIOBEACON.

To further increase the reliability of the visual radio range (directive radiobeacon) system developed by the Bureau of Standards, a course-shift indicating instrument primarily for station use has been developed and is described in the paper "A course-shift indicator for the double-modulation type radiobeacon," by H. Diamond and F. W. Dunmore in the *Bureau of Standards Journal of Research* for July, 1929. This instrument serves a two fold purpose, (1) to indicate to a station operator whether a given course as laid out in space remains unvarying during a given time of operation, and (2) to facilitate a check of the radio range calibration. A station attendant is certain that the course marked out in space remains unvarying as long as the instrument pointer is at the center scale or zero. A change in course of 0.1° is readily detected. This instrument may also be used as a visual course indicator on large aircraft. Its advantages and disadvantages as compared with the vibrating-reed course indicator are discussed.

Copies of this Research Paper No. 77 will be available within a few weeks and may be obtained from the Superintendent

of Documents, Government Printing Office, Washington, D. C. The price will be quoted by that office upon application.

RADIO DEVELOPMENTS APPLIED TO AIRCRAFT.

IN a paper "Radio Developments Applied to Aircraft" by J. H. Dellinger and H. Diamond published in *Mechanical Engineering*, July, 1929, the need for equipment and methods that will reduce the weather hazards of air transportation is pointed out. During the past three years research work carried on by the bureau has led to developments through which weather and landing conditions can be communicated to pilots while in flight and through course navigation, flying can be done satisfactorily regardless of fog. The article describes particularly the work done by the Bureau of Standards on the development of the visual radio range (directive radiobeacon) with a description of the new radio range which is capable of indicating 12 courses in space. Copies of this paper are not available from the Government.

COMPARISON OF THE FORMULAS FOR THE CALCULATION OF THE INDUCTANCE OF COILS AND SPIRALS.

IN an article entitled "A Comparison of the Formulas for the Calculation of the Inductance of Coils and Spirals Wound with Wire of Large Cross Section," by F. W. Grover, appearing in the *Bureau of Standards Journal of Research* for July, 1929, two methods have been used for the calculation of the inductance of coils of wire having a relatively large cross section. Of these, the summation method gives the inductance of the coil as the sum of the self-inductances of the turns and the mutual inductances of all the pairs of turns. The Rosa method calculates the inductance of the equivalent current sheet as a first approximation to the inductance of the coil, and obtains the correction which must be applied by calculating (*a*) the differences between the self-inductance of the turns of wire and of the current sheet, and (*b*) the differences of the mutual inductances of pairs of turns of wire and of the corresponding turns of the current sheet. It is here shown that, contrary to previous opinions, the two methods give identical

results, when terms of the same degree are retained in the series expression.

Reprints of this article, Research Paper No. 90, will be available within a few weeks and may be obtained from the Superintendent of Documents, Government Printing Office, Washington, D. C. The price will be quoted by that office upon application.

FIRE HAZARD TESTS OF JUTE.

DURING the past nine years there have occurred 112 fires aboard jute ships plying between Indian and American ports. A majority of these fires occurred after the vessel reached port and during discharge of the cargo. Since 1900 there have been reported 13 fires in jute warehouses due to spontaneous ignition.

The Marine Underwriters' Committee in coöperation with the Bureau of Chemistry and Soils of the Department of Agriculture and the Bureau of Standards is conducting an investigation of the fire hazard involved and a research associate has been assigned to work with the two bureaus on the problem. The work is proceeding along the lines of physical and bacteriological determinations.

Previous chemical analyses and tests have indicated that typical Indian jute has no spontaneous ignition hazard from the oxidation standpoint alone. Some heating by bacteriological fermentation does occur caused by cellulose splitting bacteria and resulting in the so-called "heart damage." This group of microörganisms is capable of multiplying in limited amounts of free oxygen and liberate methane and smaller amounts of hydrogen. The possible presence of other gases is being studied.

The present plan is to determine what part the microflora has in the production of secondary products of enzyme activity capable of carrying the temperature above that of the initial fermentation. The temperature and moisture conditions in ship holds give the optimum for the growth of the normal flora found on jute. While the heating thereby produced is not sufficient to cause ignition, the possible formation of unsaturated compounds and occlusion of flammable gases appear to be important.

Large heating chambers that will hold an entire bale of jute have been built and equipped with heating coils capable of maintaining temperatures up to 250° C. Means will also be provided for humidity control of the air within them and the sampling and analysis of the gases evolved. The proposed method of procedure will be to hold the temperature of the chamber a few degrees below that of the bale to provide insulation similar to that obtaining for a bale located in the middle of the ship hold. The moisture content will be altered as well as the bacterial flora of the jute bales. Many strains that have been isolated from the jute fibers and grown on artificial laboratory media will be used for the purpose. These organisms have been found to have optimum growth ranges from 20° C. to 60° C.

SMALL HOUSE SURVEY.

MATERIAL obtained from January 1 to May 15 in a recent small house survey in 31 representative cities is now being tabulated and analyzed, together with data from builders, real estate men, and material dealers. Over 400 items are included in the study of houses in each of the cities, and these should show local and nation-wide trends.

Derived data which should be of great value to the general public and to business groups will include typical room sizes, percentage of space devoted to different uses, percentage of selling price spent for lot, and selling price per square feet of floor space and per cubic foot.

Since no previous systematic study of such details is available this report should serve as a basic point of departure for further work, as well as furnish a basis for comparison in similar studies in the future.

Some of the results were made public in an address by the chief of the division of building and housing at a meeting of the homebuilders' and sub-dividers' division of the National Association of Real Estate Boards in Boston on June 26. One important conclusion was that the lowest priced houses being built commercially in most cities are of 5 or 6 rooms, with modern improvements and attractive finish, including such items as hard wood floors and built-in bath tubs. Cheaper houses can be erected, as is done in southern mill villages and

some cities which have grown most rapidly, such as Flint, Michigan, and Oklahoma City. In most cities families of low incomes apparently prefer to live in older depreciated structures rather than in new houses built at a price within their reach.

PRESERVATION OF PUBLICATIONS.

The National Research Council has received a fund of $10,000 for a coöperative investigation with the Bureau of Standards on the preservation of publications. The investigation planned consists of surveys in public libraries to find the existing conditions as to the deterioration of publications and to find means of remedying conditions found to be harmful. Consideration will be given to all materials used in books and to the influence of the atmospheric conditions in libraries. Librarians and others concerned with the preservation of valuable records published in book form have noted with considerable alarm the rapid deterioration of many such publications, and there has sprung a up general demand for accurate information which will assist in developing measures to prevent deterioration.

Test for Polarization of Electron Waves by Reflection. C. J. DAVISSON AND L. H. GERMER. (*Phys. Rev.*, May, 1929.) These two investigators have already made weighty contribution to the accumulating evidence that electrons and light waves have common properties. They now seek to find whether a beam of electrons becomes polarized when it is reflected from the surface of a nickel crystal, as light is polarized by reflection from a surface of glass. "A homogeneous beam of electrons is directed at 45 degrees incidence against a {111}-face of a nickel crystal, and the beam proceeding in the direction of regular reflection from this crystal is then reflected at the same angle of incidence from a second similar crystal. A double Faraday box is placed to receive electrons which have been regularly reflected from the second crystal, but only such electrons are allowed to enter the collector as have retained all or nearly all of their kinetic energy through the two reflections; those which have lost more than a small fraction of their kinetic energy are excluded by a retarding potential of suitable strength." The second crystal and the receiving box were rigidly connected and were rotated about the direction of the beam between the two crystals. Within the range of bombarding potentials applied there were five potentials for which the intensities of the electron beams reflected from both crystals were maxima, the reflecting faces of the two crystals being parallel. For each one of these five potentials the second crystal and the box were rotated and the current received by the box was measured as the azimuth varied. "No such variation of the current to the collector is observed within the limits of error of the measurements—about one-half of one per cent. of the total current. Our observation is that electron waves are not polarized by reflection."

G. F. S.

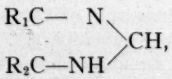
NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

ANTI-FOGGING AND ANTI-SENSITIZING EFFECTS[1]

S. E. Sheppard

In previous work with H. Hudson (*Phot. J.*, **68**: 359. 1927) it was shown that the thioanilides could act as anti-sensitizing and anti-fogging agents. It was concluded that in this case they react with silver halides in the tautomeric form

Ø representing the phenyl group and R the alkyl group. This action is now attributed to a tendency to *first form a complex silver compound with silver halide at the interface of sensitizing specks of silver sulfide with silver bromide or of silver with silver bromide.* This provides a specific chemical mechanism in explanation of Lüppo-Cramer's "nucleus isolation" hypothesis of desensitizing by dyes. It is shown that the same mechanism is applicable, completely to iminazole bodies of the type



and partially, to the phenazine dye desensitizers. In both cases the primary event in an electro-adsorption of the organic substance to silver halide at the interface of silver halide—silver sulfide or silver halide—silver, by development of a semipolar double bond, typified by $\begin{matrix}\rangle\\ \end{matrix}\!\!\begin{matrix}—N^- \ldots Ag^+\\ —C^+H \ldots Br^-\end{matrix}$. This is

* Communicated by the Director.

[1] Communication No. 342 from the Kodak Research Laboratories and published in *Phot. J.*, **69**: *37. 1929.*

followed in the case of thioanilides and iminazoles by firmer attachment of the silver ion to nitrogen, whereby these silver ions become resistant to reduction or sulfiding, so that growth of the isolated speck is inhibited. In the case of phenazine dyes, the electro-adsorption is not followed by firmer union, but oxidative attack of the speck by the dye is facilitated.

COMPARISON OF SOME DEVELOPERS FOR SENSITOMETRIC STANDARDIZATION[2]

S. E. Sheppard and A. P. H. Trivelli

THE question of a standard developer for sensitometry was discussed at the Seventh International Congress of Photography. Since *p*-aminophenol has several advantages over pyro, S. E. Sheppard proposed that it be taken as a standard developer. This proposal was adopted. The formula examined and approved is:

p-Aminophenol hydrochloride	7.25 grams
Sodium sulfite	50.00 grams
Sodium carbonate	50.00 grams
Water to	1 liter

Sensitometric comparison was made on three grades of emulsion, slow, medium, and rapid, with the proposed p.-a.-p., pyro soda, and elon hydroquinone developers. It was found that the p.-a.-p. gave equal speed, equal gammas for less fog, and somewhat lower development rate. A comparative study was made of the microscopy of the silver halide grain on development in the three developers. The transformation of the silver halide grain to silver shows three principal stages, morphologically. These are nucleation, process formation, and deformation. *p*-Aminophenol was found to give less spontaneous nucleation than the other reducers, agreeing with slighter fogging power. The photometric equivalents of the silver images produced by the developers studied were much the same at equal degrees of development.

---

[2] Communication No. 347 from the Kodak Research Laboratories and published in *Proc. Seventh International Congress Phot.*, 174 (1929).

A MACHINE FOR THE AUTOMATIC DEVELOPMENT OF SENSITOMETRIC STRIPS[3]

S. E. Sheppard and H. Crouch

NUMEROUS modern tendencies in the application of photography as a scientific tool have made it desirable that more automatic conditions be used in timing development in sensitometric work. To eliminate the personal factor and certain errors, particular attention should be paid to the method of agitation, its control, and reproducibility, and the control of time and temperature. The principle of forcing the developing solution up and down in a vertical tank has been applied in an improved form. A plunger moves up and down between the plates held in a holder. The plates are lowered into the solution by steps controlled by an automatic contact device; these development time steps being taken at right angles to the exposure steps. A final contact on the control tape or cam operates large discharge and wash valves. The apparatus is arranged for operation in an inert atmosphere if desired. Photometric data show that the uniformity of development reached is as high as the emulsion coating permits.

[3] Communication No. 348 from the Kodak Research Laboratories and published in *Proc. Seventh International Congress Phot.*, 201 (1929).

Use of Aluminium in the Marsh Test. ELMER B. SVENSON. (*Chemist-Analyst*, 1929, *18*, No. 3, 5) recommends the use of metallic aluminium, in the form of rod, instead of zinc in the Marsh test for arsenic. The aluminium is entirely free from arsenic, and readily reacts with hydrochloric acid to produce nascent hydrogen. When sulphuric acid is used, the aluminium should be activated by immersion in a slightly acid solution of a salt of copper or mercury until a light coat deposits on the rod. Copper-coated rod may be dried and stored. Mercury-coated rod is more active, but must be freshly prepared. The Marsh test, thus modified, gives accurate and sensitive results.

J. S. H.

Quantitative Determination of Sodium. EARLE R. CALEY AND C. W. FOULK, of Ohio State University (*J. Am. Chem. Soc.*, 1929, *51*, 1664–1674) determine sodium, both gravimetrically and colorimetrically, as the crystalline triple acetate of sodium, magnesium, and uranyl, which has the formula $NaC_2H_3O_2 \cdot Mg(C_2H_3O_2)_3 \cdot 3UO_2(C_2H_3O_2)_2 \cdot 6\frac{1}{2}H_2O$. The reagent is the double acetate of magnesium and uranyl dissolved in 6 per cent. acetic acid. The solution containing sodium, preferably as its chloride, is concentrated to a small volume, say 5 cc. or less if no salts separate. The reagent is added rapidly. The resulting solution is mixed, cooled to a temperature of 20° C., and then stirred vigorously for one-half to three-fourths of an hour. The triple acetate separates, is immediately collected on a Gooch crucible, washed with 95 per cent. alcohol, dried for 30 minutes at a temperature of 105° to 110° C., cooled, and weighed. The determination may also be made colorimetrically. The washed precipitate of triple acetate is dissolved in water which is poured into the Gooch crucible. The resulting yellow solution is diluted to a definite volume, and compared in a colorimeter with a standard solution of the triple acetate. The amount of sodium in the unknown is then calculated.

J. S. H.

THE FRANKLIN INSTITUTE.

MEMBERSHIP NOTES.

CHANGES IN ADDRESS.

MR. HERBERT S. BERLINER, c/o The Compo Company, Ltd., 131 Eighteenth Avenue, Lachine, Quebec, Canada.

MR. STERLING H. BUNNELL, Industrial Department, The National City Company 55 Wall Street, New York City.

MR. ARTHUR L. Church, 123 South Broad Street, Philadelphia, Pa.

MR. ROLAND B. DAY, 1126 Subway Terminal Bldg., 417 South Hill Street, Los Angeles, California.

MR. JAMES J. FITZPATRICK, 923 North Sixty-fifth Street, Philadelphia, Pa.

DR. ROBERT GRIMSHAW, 1040 Nelson Avenue, New York City, N. Y.

MR. GEORGE KRAUSS, 8019 Hillcrest Avenue, Elkins Park, Pa.

DR. GEORGE F. STRADLING, Apartment 302B, The Kenwood, 247 West Tulpehocken Street, Germantown, Philadelphia., Pa.

NECROLOGY.

Mr. Emile Berliner, Washington, D. C.

LIBRARY NOTES.

RECENT ADDITIONS.

CAJORI, FLORIAN. A History of Mathematical Notations. Two volumes. 1928–29.

Fuel Conference—World Power Conference. Transactions 1928. Four volumes.

GEIGER, H., AND KARL SCHEEL, editors. Handbuch der Physik. Vol. IV. 1929.

JAMIESON, GEORGE S. Volumetric Iodate Methods. 1926.

LILLEY, ERNEST RAYMOND. The Geology of Petroleum and Natural Gas. 1928.

Philadelphia City Directory 1929.

SMITH. D. M. Visual Lines for Spectrum Analysis. 1928.

STEEL, MATTHEW. Physical Chemistry and Biophysics. 1928.

WIEN, W., AND F. HARMS, editors. Handbuch der Experimentalphysik. Vol. 13, part 3. 1929.

BOOK REVIEWS.

THE GEOLOGY OF PETROLEUM AND NATURAL GAS. By Ernest Raymond Lilley, Sc.D., Associate Professor of Geology at New York University, Author of "The Oil Industry," x–524 pages, 173 figures, 62 tables. New York, D. Van Nostrand Company, Inc., 1929. Price $6.

To the State of Pennsylvania belongs the distinction of having the first oil well drilled within its boundaries. This well was sunk near Titusville, Pa., in 1859 under the direction of Colonel Drake and reached a depth of 69 feet. Due to the successful development of the internal combustion engine the oil industry in the past seventy years has risen from nothing to a world production of over a billion and a quarter barrels per year. This industry with its enormous and rapid development has afforded a wholly new field for the practical application of the science of geology.

Probably no one realizes more fully than the author just how extensive has been the work and study on the geology of petroleum and natural gas up to the present time. In a book this size he has been obliged to forego inclusions from the wealth of available descriptive data and confine himself "to brief statements of the principles of the science and examples illustrative of the application of those principles." The first few chapters deal with the origin of petroleum and the general properties of it and related mineral bitumens. The origin of petroleum has been a much debated question and one which held the interest of scientists in general. The organic in preference to the inorganic is widely accepted but, as to whether of animal or vegetable origin, or, just how the transformation to petroleum took place, each theory has numerous supporters. Following these preliminary chapters there is a discussion of the fundamental geologic conditions limiting the occurrence of petroleum, the existence of these conditions as evidenced by the occurrence of oil in geologic strata of various ages and the structural nature of these oil containing rocks. Several explanations have been advanced to account for the accumulation and concentration of oil and gas in certain spots. According to the author the gravitational theory offers the most logical explanation. The correlation between structural conditions and the occurrence of oil was largely begun by Dr. I. C. White who, in 1885, published a theory that the ideal location of a petroleum reservoir was the crest of an anticline. That this is true to a limited extent only is shown by the latter half of the book which describes an extensive variety of geological formations found in conjunction with producing oil wells. It is obvious that important parts also are played by faulted structures, variations in porosity, extrusions of igneous rocks, salt core structures and various unconformities between strata. The final chapter on the exploration of new areas will be of particular interest to the reader. The use of geophysical methods of exploration is more or less in its infancy. So far, the best results have been obtained with the gravity balance and the seismograph. Magnetic and electric methods as well as radio wave utilization await further developments before they can be of much practical value.

The book is a very comprehensive summary of all the phases of geology in its relation to petroleum. As intended, the student of the geology of petroleum should find this the means of obtaining an excellent grounding in the subject.

T. K. CLEVELAND.

DIE SPEZIELLE RELATIVITÄTSTHEORIE EINSTEINS UND DIE LOGIK. By Dr. J. H. Tummers, University of Nymegen. Second, revised and augmented edition. Pamphlet, 32 pages, 8vo. Leipzig, Otto Hillmann, 1929.

Relativity is still a moot question, although those who work in the higher levels of physics and mathematics seem to be mainly in favor of it. The essay in hand was first published in 1924, in German, appeared in French in 1925, and now appears in German in a revised, improved form. The prime position of the author is that the fundamental principles (the constancy of the speed of light and the principle of relativity) are postulates. A new chapter has been added in which it is sought to reconstruct the theory of Einstein free from logical objections. The author has made also special effort to protect the theory from illogical details. Through these attempts he has arrived at the contraction hypothesis of Lorenz. A new introduction has been written in which is discussed the difficulties that have arisen in consequence of the discarding of the theory of the ether, that mysterious medium which has so long dominated physical science.

The pamphlet is written in excellent German, clearly printed, and is well worth perusal by those favorable or unfavorable to the theory of relativity, as Einstein propounds it.

H. L.

PROCEEDINGS OF THE SEVENTH INTERNATIONAL CONGRESS OF PHOTOGRAPHY. Held in London, England, July 9–14, 1928. Edited by W. Clark, T. S. Price and B. V. Storr. 571 pages, illustrations, 8vo, cardboard binding. Cambridge, W. Heffer & Sons, Ltd., 1929. Price, 25 shillings.

Could Heinrich Schulze return he would certainly be amazed at the extent of the art and science that has grown out of his crude experiment a little over two centuries ago. Printing has been called the art preservative of all arts, and Gibbon, in speaking of the destruction of manuscripts at the taking of Constantinople in 1453, says that fortunately "the mechanics of a German town had invented an art that enables literature to defy the ravages of time and barbarism." Photography is much superior to ordinary printing in the matter of preserving earlier writings. The photographic copying of important and unique MSS. has enabled scholars to obtain all the advantages of consulting such records without journeying to the place of deposit. Another important and useful application of the photograph is the instrument by which copies of scientific and historical publications may be obtained accurately and at small cost, thus giving the research worker free access to original records and sparing libraries the risk and inconvenience of loaning their treasures.

The papers presented to the Congress cover, as would be expected, a wide range. There are so many applications of photography, so many questions of technic and so many problems in the chemistry and physics of it, that ample scope for investigation and also for difference of interpretation is offered and many moot points are and will be subjects of discussion. The nature of the latent image is discussed in a paper of considerable length and allusions to the question are found in other papers. The general tendency is as would be expected, to base the explanations on the modern recondite theories of physical chemistry. Insufficient attention is given in these discussions to the possibility of development after fixing, since the whole of the silver halide may be removed immediately after exposure

and the image still obtained, either at once or after a long interval. These facts are recorded in standard photographic literature yet seem to be overlooked; the procedures are of little value, but they are interesting as peculiarities of the action of light.

The desensitizing of panchromatic plates is discussed in an elaborate and valuable contribution. That certain substances, *e.g.*, potassium iodide, will diminish the sensitiveness of the silver halides has long been known, but it was less than a decade ago that Lüppo-Cramer announced the discovery of the action of phenosafranin as a prompt and efficient desensitizer. The discovery was received with astonishment and gratification by photographers all over the world, for it afforded relief from the disagreeable conditions under which the panchromatic plate must be developed. As usual in such cases, it was soon found that other dyestuffs had similar properties, and several of more satisfactory type were introduced. A considerable number of these are now available and find wide application. The paper on the subject is comprehensive, presenting the theory as well as the practise of the procedure, giving the structural formulas and important relations of the compounds in use. It is pointed out that the desensitizers now on the market are mostly the commercial forms, not guaranteed as to purity, and it behooves investigators of this subject to endeavor to study the action of compounds of perfectly definite character. By this means alone can trustworthy data, positive or negative, be obtained. To review the desensitizing action of the thousands of compounds now known derived from coal-tar seems, as the author says, like looking for the proverbial needle in the haystack, but there is a reasonable prospect that some compounds more suitable for the purpose than those so far known may be found.

The volume contains a vast amount of valuable information on the important phases of photography. Reference to the data is greatly facilitated by a good index. A photogravure of the assembled members of the Congress is attached, from which it is seen that almost all present were from Great Britain and Germany. Only one representative from the United States is present, Dr. Sheppard of the Eastman Company.

HENRY LEFFMANN.

THE PRINCIPLES OF PETROLOGY. An Introduction to the Science of Rocks. By G. W. Tyrrell, A.R.C.Sc., F.G.S., F.R.S.E., Ph.D. (Glasgow), Lecturer in Geology in the University of Glasgow. xii–349 pages, 78 figures, New York, E. P. Dutton and Company. Price, $3.25.

Students of geology in general and petrology in particular will appreciate in full the task Professor Tyrrell has undertaken. In this book a particularly successful attempt has been made in summarising modern petrology from the genetic standpoint. Rocks are classified under three main headings: Primary or Igneous, Secondary (sedimentary, etc.), and Metamorphic. Each type is elaborated in its turn. Most important are the igneous rocks. In these all other types have their origin. The author begins with a description of the composition and constitution of magmas and employs well-known physico-chemical principles to show how the various kinds of rocks are gradually evolved from the slow cooling magma. A study of crystal form and composition has made much of the process of rock formation an open book. Secondary rocks may be of

sedimentary, chemical or organic origin. The author has taken pains to describe the various types as evidence of their characteristic modes of formation. The sedimentary rocks also are classified according to causal origin and fall under such headings as cataclastic, thermal, dynamothermal, plutonic, etc.

The author seems to have covered his subject pretty thoroughly. In addition to a masterly treatment of the process of rock genesis and formation the book is a veritable glossary of petrological terms which enhances its value to students as a reference work but might appear to the layman as a paradise for composers of crossword puzzles and cryptograms.

T. K. CLEVELAND.

PUBLICATIONS RECEIVED.

Exact Colour Matching and Specifying, by L. Blin Desbleds. 116 pages, illustrations, 12 mo. Paris, Technological and Industrial service, no date, price $1.00.

Die Spezielle Relativitätstheorie Einsteins und die Logik, von Dr. J. H. Tummers. Zweite, vermehrte und umgearbeitete Auflage. 32 pages, illustrations, 8vo. Leipzig, Otto Hillmann, 1929.

Canada, Department of Mines, Mines Branch. Investigations in Ore Dressing and Metallurgy, 1927. 186 pages, illustrations, plates, 8vo. Ottawa, King's Printer, 1928.

Ontario Department of Mines. Thirty-seventh annual report, 1928, vol. 37, part iv. 160 pages, illustrations, plates, maps, 8vo. Toronto, King's Printer, 1929.

Bureau of Science, Philippine Islands. Twenty-sixth annual report, including excerpts from the twenty-fifth annual report, to the honorable Secretary of Agriculture and Natural Resources by William H. Brown, director of the Bureau for the year ending December 31, 1927. 81 pages, 8vo. Manila, Bureau of Printing, 1929.

Energie und Wirtschaft, von Ing. Fr. Brock. 39 pages, illustrations, plates, 8vo. Wien, Oesterreichischer Ingenieur und Architekten Verein, 1929, price 3.50 marks.

Bell Telephone Laboratories, Reprints: No. B-373, Ground return impedance by John R. Carson, 5 pages, 8vo. B-375, New method for obtaining transient solutions of electrical networks by W. P. Mason. 26 pages, illustrations, 8vo. B-376, Acoustic considerations in steady state loud speaker measurements by L. G. Bostwick. 24 pages, illustrations, 8vo. New York, American Telephone and Telegraph Company, 1929.

National Advisory Committee for Aeronautics. Technical Notes: No. 311, The use of wheel brakes on Airplanes by Thomas Carroll and Smith J. De France. 9 pages, diagrams, photographs, quarto. Washington, Committee, 1929.

Loxite, description of the perfected liquid oxygen explosive. 20 pages, illustrations, quarto. Chicago, Keith Dunham Company, 1929.

CURRENT TOPICS.

Discussion on the Structure of Atomic Nuclei. Opened by SIR ERNEST RUTHERFORD. (*Proc. Roy. Soc.*, A 792.) At the meeting of the Royal Society on February 7, 1929, the president, Sir Ernest Rutherford, directed attention to a similar meeting held fifteen years ago to consider the constitution of the atom. He opened the discussion and was followed by Silvanus P. Thompson, Stanley Allen, Professors Soddy, Hicks, Nicholson and Mr. Moseley, who was afterward killed on the Gallipoli expedition. Professor Soddy spoke of isotopes and presented evidence to show that neon might consist of a mixture of isotopes. Mr. Moseley told of his X-ray investigations by which the atomic numbers of the elements were determined. In the course of the fifteen years between the two meetings three new methods have been devised to attack the problem of the structure of the nucleus itself.

1. Proof has been furnished of the isotopic composition of many elements and the masses of the several isotopes have been measured chiefly by Aston. Moseley fixed the possible number of nuclear charges while Aston has demonstrated by experiment the existence of isotopes of the same element, all of which have the same nuclear charge though they differ in mass and nuclear composition. The early work of Aston made clear that the atomic masses of the elements, each isotope being regarded as an element, are expressed as whole numbers to a close approximation when the mass of oxygen is taken as 16. "The evidence from isotopes and from the artificial disintegration of light elements shows fairly clearly that the mass units entering into the composition of the nucleus have a mass in the nucleus of about 1. This unit has been named the proton, and we believe that the proton is identical with the hydrogen nucleus when in the free state." By itself a proton has a mass of 1.0073 in terms of O = 16, but in a nucleus its mass is nearly 1. "This difference in mass between the free and nuclear proton is ascribed to this packing effect, *i.e.*, to the interaction of the electromagnetic fields of the protons and electrons in the highly condensed nucleus. On modern views, we know that there is a close relation between mass and energy and a decrease in mass means a loss of energy. This apparently small loss of mass means that a large amount of energy has been emitted in the entrance of the free proton into the structure of the nucleus, an amount corresponding

to about 7 million electron-volts." If we assume that the nuclei of other elements are made up of groups of electrons and protons the deviation of their atomic masses from whole numbers indicates the importance of the packing effect. For elements in the neighborhood of tin with an atomic weight of about 120 the departure of the mass from the whole number rule is a minimum. "In forming an atom of mass 120 containing 120 protons, energy has been lost corresponding to 840 million volts, and this energy has been probably radiated away into space. On such a view it is clear that the atom, instead of being as ordinarily supposed a store of energy, is really a sink of energy; and if we took the nucleus of mercury, for example, to pieces, proton by proton, we should have to do an enormous amount of work corresponding to at least 1400 million volts." On the other hand let it be supposed that not protons but helium nuclei are the units in the structure of the nuclei of atoms with large atomic weight. In the formation of a helium nucleus from four protons and two electrons a loss of mass and a consequent radiation of energy has already occurred. In the free state the nuclear mass of helium is 4.0018. From tin on up to uranium the increase in atomic weight corresponds to the addition of helium nuclei having a mass of about 4.005. This accretion of mass is sufficient to account for the energy that radioactive elements have to emit.

2. The second method is that of the disintegration at will of the elements by alpha ray bombardment. Thus it is possible to change artificially the structure of nuclei. When disintegration is effected a proton is emitted at a high velocity. "It is noteworthy that while the radioactive substances spontaneously break up always with the emission of helium nuclei or electrons, in the artificial disintegration of the lighter atoms no helium nuclei, so far as we know, are liberated, but a proton is set free."

In the discussion Dr. Chadwick, who has collaborated with Professor Rutherford in his disintegration studies, brought forward additional considerations. The protons liberated by bombarding the lighter elements with alpha particles are detected by the scintillations they produce on a zinc sulphide screen. "The disintegration is supposed to occur when an α-particle penetrates into a nucleus and is captured by it, the result of the capture being the emission of a proton. The chance of disintegration is small; in the favorable case of nitrogen, for example, about 20 nuclei are disintegrated for every 10^6 α-particles in the incident beam." All elements from boron to potassium inclusive, except carbon and oxygen, have been artificially disintegrated and send out high speed protons. Thus it is known that their nuclei contain protons. In

some disintegrations the liberated protons have more energy than the incident α-particles, the process being accompanied by a release of energy. "There is a striking difference in behaviour between the elements of even atomic number and those of odd atomic number; the protons liberated from the odd-numbered elements have greater maximum energies than those from the even elements. The difference in behaviour of odd and even elements therefore suggests, in agreement with the evidence from relative abundance and from atomic masses, that the even elements are more stable than the odd."

3. The third line of approach has been by studying the gamma rays emitted by the nucleus under disintegration. Dr. Ellis, who was the first to measure the wave-length of these rays, later found that they are more commonly associated with disintegration accompanied by the emission of beta rays. "They can be considered as the characteristic spectrum of the nucleus and their emission is due to the disturbance caused by the departure of the α- or β-particle." They are homogeneous to $\frac{1}{10}$ per cent. It seems unlikely that either electrons or protons could emit such homogeneous high frequency radiation. Their origin is therefore to be sought in α-particles or in the nucleus as a whole, perhaps in rotation. Preliminary experiments have been made that promise to add much to what is known of the source and nature of these rays. O. W. Richardson presented an *a priori* argument for the rotation of nuclei in some instances, and also stated that good spectroscopic evidence of the rotation of the nuclei exists. In his presentation of the problems of the nucleus Sir Ernest Rutherford took up the studies made by himself and Dr. Chadwick on the dimensions of nuclei and on the laws of force that prevail near to them. Upon the nature of these laws much information has been obtained by studying the scattering of α-particles when an intense beam of them falls on a thin sheet of matter. "When we examine all elements, from copper of atomic number 29 to uranium of number 92, it is found that the scattering is normal; that is to say, that the scattering agrees within experimental error with what we should expect if the law of inverse square holds in the region which is penetrated by the α-particle." In the case of the scattering produced by lighter elements, such as aluminium and magnesium, different results are obtained which cannot be interpreted so simply. "The most natural explanation, and one which I think fits in well with the results, is to suppose that, in addition to the ordinary repulsive forces of the electric type between the nuclei, at close distances attractive forces come into play, so that the resultant force is a combination of the forces of repulsion and attrac-

tion." On the assumption that the force of attraction varies inversely as the fifth power of the distance the observed scattering due to aluminium is in fair agreement with calculation.

G. F. S.

The Measurement of Flame Temperature. EZER GRIFFITHS AND J. H. AWBERY. (*Proc. Roy. Soc.*, A 792.) "To define the 'temperature' of a flame, and to be sure that the concept has a unique meaning, is no easy task." The authors have found no definition that they can accept and recommend without reservation but, as a working definition, they propose this: "The temperature of a flame is the temperature of a solid body which is in thermal equilibrium with the flame."

Early workers inserted a solid object into the flame, often a thermocouple, and estimated its temperature. The temperature of the flame was, however, lowered by the inserted solid. The authors have devised a more accurate method. Let a wire carrying an electric current be inserted in a flame. Under steady conditions heat escapes from the wire in three ways: "(1) Part is radiated to distant cool objects; (2) part is conducted along the wire to its supports, and eventually reaches the air; (3) part is transferred to the hot gases composing the flame. Now if the wire is at the temperature of the flame, the last action cannot take place, and all the heat generated is either radiated or conducted away. A similar condition prevails, however, if the wire is in a vacuum, since in this case there is no convection. Thus if the point is found at which both the current and the temperature are the same for the wire in the flame and in a vacuum, this temperature will be the flame temperature; for the equality of temperature ensures that the radiation and conduction terms shall be equal in the two cases, whilst the equality of current ensures that the total heat dissipated is unaltered. Hence the remaining term (convection) is equal in both cases and, since it is zero in the vacuum, it is also zero in the flame, so that the wire is at the flame temperature." In applying this method to the measurement of the temperature of a Meker flame a platinum wire carrying an adjustable current was set up in turn in the flame and in a bell jar exhausted to below $\frac{1}{10}$ mm. mercury pressure. For each strength of current in the wire its temperature was measured by a disappearing filament optical pyrometer. The curves, practically straight lines, were plotted connecting amperes and temperatures Centigrade. In the vacuum the temperature rose much more sharply with increasing current than in the flame. Thus in the flame an increase of two amperes was needed to raise the temperature from 1575°

to 1775°, while in the vacuum to produce the same change the addition of about .4 ampere sufficed. The two lines crossed at 1775°, the current in both cases then being 3.1 amperes. Certain sources of error were considered and obviated. In the case of a different flame the temperature as measured by the above method with a rhodium wire, which has a higher melting point than platinum, was found to be 1877° with wire .5 mm. diameter and 1886° with wire .2 mm. diameter. In addition to the method already described a "Method of Spectral Line Reversal" is given. If white light be sent through a sodium flame, and its spectrum be formed, the D lines of sodium will depend for their appearance on the relative temperatures of the light source and of the flame. If the source is the hotter, the lines are dark. If the flame is the hotter, the lines are bright against the background of the continuous spectrum, but if flame and source have the same temperature, the lines merge into the adjacent spectrum. Fery used this principle in his absorption pyrometer.

In practice the source of white light was the incandescent sphere of tungsten in a tungsten arc, the Pointolite lamp. The light traversed a flame fed steadily with a sodium chloride solution, whose concentration had no influence on the temperature found. The emergent light was received by a spectroscope. The current in the tungsten arc was varied by a rheostat until the sodium lines seen in the spectroscope were neither brighter nor dimmer than the adjacent parts of the spectrum. The temperature of the tungsten sphere was then got by the pyrometer. In this way the temperature of the flame already measured as 1877° and 1886° was found to be 1883°, though the authors claim that the excellent accord is accidental. With another flame the temperature with the sodium lines came out 1736° and with lithium lines 1730° C. When sodium and lithium lines were used together they were seen to disappear and to reverse simultaneously.

The vertical distribution of temperature in a Meker flame 14 inches high was studied by the reversal method,

Distance above base of flame.....	1	2	3	4	5	6	7
Temperature.....	1780°	1790	1755	1665	1660	1650	1600?

In the usual methods of measuring the temperatures developed in gaseous explosions much difficulty is encountered because the maximum temperature lasts for only a brief time. The sodium reversal method surmounts this. A mixture of CO, air and N_2 was exploded in a bomb provided with two windows for the passage of light from the Pointolite lamp. Sodium carbonate was scattered

in the bomb to provide the lines to be observed. Before explosion there was a continuous spectrum. Upon explosion the D lines appeared dark and, later, they flashed up bright, provided the arc of the lamp was cooler than the gases developed. It was possible to adjust the temperature of the arc until the lines just about appeared when the explosion came. Thus within an error of 10° the temperature within the bomb was found to be 2100° C. By the reversal method the temperature of a flame of atomic hydrogen was determined four times with these results, 2525°, 2490°, 2540° and 2515° C.

G. F. S.

The Figure of the Earth Derived by Triangulation-Methods. WILLIAM BOWIE. The Figure of the Earth from Gravity Measurements. C. H. SWICK. (*Am. J. Sci.*, July, 1929.) The oldest method of finding the figure of the earth depended on measuring the angular distance between two places by astronomical means and the linear distance by some direct method. About 300 years ago triangulation was resorted to for getting the linear distance. Since it was hard to determine astronomic longitude with accuracy the stations used were selected on the same meridian. When, at the middle of the last century, the electric telegraph made astronomic longitudes possible of exact measurement, it was no longer necessary to limit triangulation to a north and south line. C. A. Schott in the U. S. Coast and Geodetic Survey used an arc of the 39th parallel of latitude and also an oblique arc from Maine to Alabama to get the figure of the earth. "It is believed that the late Professor John F. Hayford, while in the United States Coast and Geodetic Survey, was the first to use a large connected system of triangulation, involving arcs along meridians, parallels of latitude and oblique arcs, in the determination of the figure of the Earth. His method proved to be so successful that it is reasonably certain that hereafter it will be used almost exclusively."

The weakness of the triangulation method is this: Of the 197,000,000 square miles of the earth's surface only 57,000,000 is land and of this but a small part has been covered by triangulation. The entire United States covers less than two per cent. of the area of the globe. Can conclusions drawn from so small a part be extended to the earth as a whole? In the triangulation net in the western U. S. the error in closure of circuits was one part in 450,000. "The perimeter of the entire system of triangulation was 5300 miles and the closing error was only 34 feet or one part in 840,000." For the circumference of the earth this error would be about 500 feet.

The errors in the astronomical determination of latitude amount to 0.1″ or less and for longitude to 0.25″, or to approximately 10 and 20 feet respectively. These errors are greatly outweighed by those due to the irregular surface of the earth and to variations in the density of the outer portion of the earth. Hayford used the principle of isostasy to avoid these latter errors, assuming "that any prism of the Earth's crust, of a given cross-section, contains the same mass as any other prism of the crust of equal cross-section. This presupposes that the density under an area of low elevation is greater than that under an area of high elevation." Applying this principle he corrected astronomical observations for the attraction of matter above sea-level, for the low density of the oceans in comparison with the earth as a whole, for the lower density under land masses and for the greater density under water areas. He thus obtained more exact values of the dimensions of the earth than had hitherto been determined. Gravity data obtained by Meinesz on a voyage in a submarine from Java to Holland confirm results based on isostasy.

The triangulation of the United States is being extended. In the east it is likely that it will connect with the Canadian system, and in the south the Mexican arcs may be utilized.

Somigliana has claimed that the size of the earth as well as its shape can be inferred from the results of gravity measurements, but this is true to only a limited extent. Such measurements are used to calculate the flattening of the earth at the poles. At the equator the acceleration of gravity is 978 cm. per sec. per sec., while at the pole it is 983. The change is thus only 5 parts in 1000 along a quadrant of the earth. Even this small change must be attributed to the shape of the earth and to its centrifugal force jointly, so that extreme accuracy is essential if conclusions are to be drawn. Indeed an error of less than one part in a million is very desirable. The intensity of gravity at any place depends on the total mass of the earth, the distance from the center of the earth, the centrifugal force of rotation and on the distribution of mass around the selected spot. Local distributions of matter are often unknown and yet they affect the intensity of gravity. The isostatic method furnishes a good solution of such problems. "When we have gravity-stations, therefore, that have been isostatically reduced we do not have to select particular stations for figure-of-the-Earth computations. We can use any or all of the stations, without fear of introducing large errors into our work."

It costs less to find the shape of the earth by gravity determinations than by triangulations and astronomical measurements.

Much money was spent in the eighteenth century in measuring arcs for investigating the figure of the earth.

Ten years ago there were in the United States 220 gravity stations and Bowie gave 297.4 as the reciprocal of the flattening derived from these. Now there are 100 more. More recently Hayford has given for this value 297, deriving it from deflections from the vertical. 297 was adopted at the Madrid conference for the International Spheroid.

"Our greatest need at present though, as regards the fundamental problem of the figure of the Earth, is a gravimetric survey of the oceans. There are at present only about 200 satisfactory gravity determinations over the oceans, all of which are due to the efforts of one small country, Holland." Accurate geodetic surveys have been made over about one-tenth of the surface of the earth. Any data for the water areas is very recent. Conclusions for the whole earth based on an examination of so small a part of its surface must be received with great caution. Helmert, Heiskanen and others have drawn the conclusion that the mean figure of the earth is an ellipsoid of three unequal axes and not an ellipsoid of revolution. Already the extension of observations to include oceanic areas has thrown doubt on this deduction. Thus Holland once more has played a part in the field of science quite out of proportion to her size.

G. F. S.

Vegetable Foods as a Source of Iodine. ROE E. REMINGTON. (*Science*, 1928, *68*, 590) calls attention to vegetables as a source of iodine in the diet. Vegetables grown in South Carolina have a comparatively high iodine content. A four-ounce potato contains sufficient iodine to satisfy the daily requirement of that element by a man. The leafy vegetables are also excellent sources of iodine.

J. S. H.

Test for Lactic Acid. H. V. ARNY AND MARGUERITE C. DIMLER. (*J. Am. Pharmaceutical Asso.*, 1929, *18*, 459–462) recommend the following test for the detection of the presence of lactic acid in a solution. The lactic acid is removed by shaking the solution with an equal volume of ethyl acetate. Three successive extractions may be made. The ethyl acetate is separated, washed, first with distilled water, than with dilute sulphuric acid, filtered, and evaporated on the water bath. The residue is a syrup. It is dissolved in 5 cc. of a 1 per cent. solution of resorcinol. The resulting solution is placed over 5 cc. of concentrated sulphuric acid, so that a

"ring test" results. After 2 minutes, the tube is rotated gently; a red color indicates the presence of lactic acid.

J. S. H.

Platinum in Washington. J. T. PARDEE. (U. S. Geol. Survey, Bull. 805A, 1–15, 1928) has studied the reported occurrence of platinum in the black sand of the state of Washington. A total production of approximately 7.5 ounces of platinum from that state has been reported. Profitable exploitation of the deposits is difficult since they lack uniformity in occurrence and in metallic content; and the expense, involved in mining the raw material and then treating it, is too great.

J. S. H.

Anthracite Sizes for Domestic Use. R. H. FERNALD. (Rep., Mechanical Engineering Dept., Towne Scientific School, Univ. Pennsylvania, 1928, 75 pages) describes a research conducted by that department on Anthracite Sizes for Domestic Use. The general conclusions may be summarized. Standard commercial egg size coal is least efficient. The run of mine coal, from egg to buckwheat inclusive, is best for average heaters, while a mixture of two-thirds chestnut and one-third pea and buckwheat is best for average size ranges. Adequate heater capacity, uniform fuel quality, and, above all, clean coal, which is low in ash and free from serious clinkering ingredients, are of far greater importance to the householder than anthracite sizing.

J. S. H.

Relative Humaneness of Chemical Warfare. COL. HARRY L. GILCHRIST, of the Medical Corps, U. S. Army and Chief of the Medical Division of the Chemical Warfare Service, is the author of a monograph entitled "A Comparative Study of World War Casualties from Gas and Other Weapons" published by the Chemical Warfare School, Edgewood Arsenal, 1928, 51 pages. The concluding chapter of this monograph demonstrates that gas warfare is more humane than warfare waged with other weapons. Gas causes less suffering than wounds. If a man becomes a casualty from gas, his suffering is less severe and of shorter duration than if he were wounded by other war weapons. With the lung irritants, the exposed man is fairly out of danger at the end of 48 hours. The burns produced by mustard gas are not painful after the first 24 hours, although the patient may be hospitalized for several weeks. The mortality among gas casualties is far less than among casualties from other weapons. When those killed in

action are excluded from the statistics, it is then found that the per cent. of the gas casualties who died was: British Army 3.3, German Army 2.9, United States Army 2. The per cent. of casualties from all other weapons who died was: British Army 36.6, German Army 43, United States Army 24.

J. S. H.

Memorial Service for Edgar Fahs Smith. The proceedings of the memorial service for the late Provost Smith, held under the auspices of the University of Pennsylvania on December 4, 1928, have been published as a brochure of 62 pages. It contains the addresses by Francis Xavier Dercum, Marston Taylor Bogert, and Josiah Harmar Penniman, the invocation and the benediction by Richard Montgomery, a picture and biographical summary of Dr. Smith, and a bibliography of his publications and of the doctoral theses prepared under his direction.

J. S. H.

Atomic Weight of Nickel. GREGORY PAUL BAXTER AND SABURO ISHIMARU (*J. Am. Chem. Soc.*, 1929, *51*, 1729–1735) have compared the atomic weights of terrestrial and meteoric nickel. They find that nickel extracted from a new meteorite has the same isotopic composition as terrestrial nickel. By the analysis of nickelous bromide, they obtain 58.694 as the atomic weight of nickel. The average value of the most recent determinations of this constant is 58.697.

J. S. H.

Health Hazards in Chromium Plating. J. J. BLOOMFIELD AND WILLIAM BLUM (Public Health Reports, 1928, *43*, 2330–2351) have made a study of several chromium plating plants. They find that a real, though not critical, hazard exists in this industry. Inflammation of the nasal tissues and even perforation of the nasal septum may occur. The digestive system and the respiratory system are not injured. Continuous daily exposure to concentrations of chromic acid greater than 1 milligram per 10 cubic meters of air is likely to exert an injurious action on the tissues of the nose. Neither natural nor vertical ventilation is effective in removing the chromic acid spray which is produced during plating. Transverse ventilation should be used, drawing the air laterally across the surface of the tank into ducts at its top. These ducts should be 1 to 2 inches wide and extend the entire length of the tank. Each duct should not draw air for a lateral distance in excess of 18 inches. The air should have a velocity of approximately 2000

feet per minute at the duct. The level of the plating solution should be at least 8 inches below the top of the tank. The workmen should wear rubber boots, gloves, and aprons, protect the nasal tissues by application of a suitable salve, and submit to periodic medical examinations.

J. S. H.

New Canadian Journal. On May 1, the National Research Council of Canada published the first number of the *Canadian Journal of Research*. This journal will be devoted to suitable papers by Canadian research workers, primarily in chemistry, physics, and biology, although other branches of science will be included. For the present, bi-monthly numbers are issued; but the journal will appear monthly in the near future. The first number contains three papers on rust resistance in wheat, one on the aluminates of calcium, one on vaccination against tuberculosis, and one on the action of ultra-violet light on certain marine organisms. These communications make an excellent number of 109 pages.

J. S. H.

THE FRANKLIN INSTITUTE

OFFICERS FOR 1929

President	NATHAN HAYWARD
Vice-presidents	HENRY HOWSON C. C. TUTWILER WALTON FORSTALL
Secretary	HOWARD MCCLENAHAN
Assistant Secretary and Librarian	ALFRED RIGLING
Treasurer	BENJAMIN FRANKLIN
Controller	WILLIAM F. JACKSON, JR.

Board of Managers

JAMES BARNES
GEORGE H. BENZON, JR.
CHARLES E. BONINE
EDWARD G. BUDD
FRANCIS T. CHAMBERS
G. H. CLAMER
THEOBALD F. CLARK
WALTON CLARK
MORRIS L. CLOTHIER
THOMAS D. COPE
CHARLES DAY
ARTHUR W. GOODSPEED
CLARENCE A. HALL
GEORGE A. HOADLEY
ROBERT W. LESLEY
MALCOLM LLOYD, JR.
MARSHALL S. MORGAN
CHARLES PENROSE
JAMES S. ROGERS
GEORGE D. ROSENGARTEN
E. H. SANBORN
HASELTINE SMITH
SAMUEL T. WAGNER
J. T. WALLIS
WILLIAM C. WETHERILL